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THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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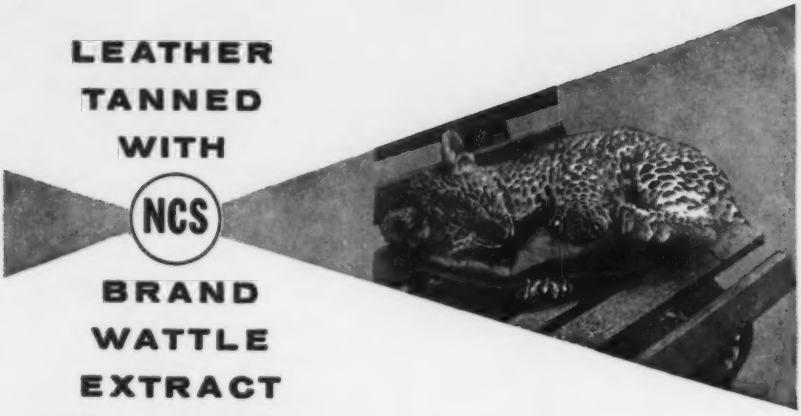

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The Journal
of the
AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIV OCTOBER 1959 No. 10

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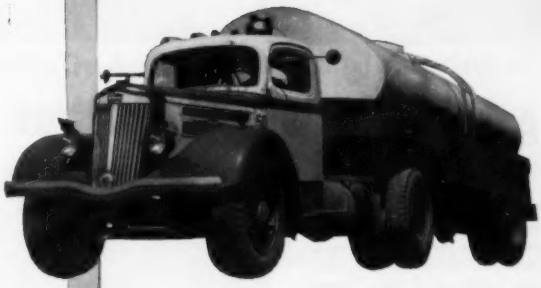

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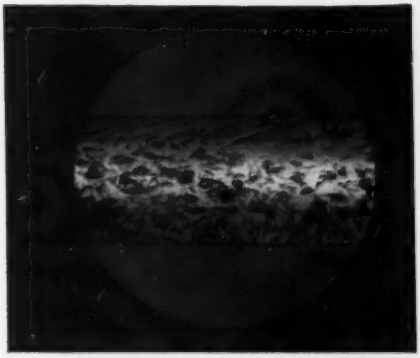

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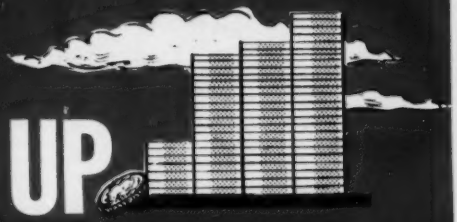

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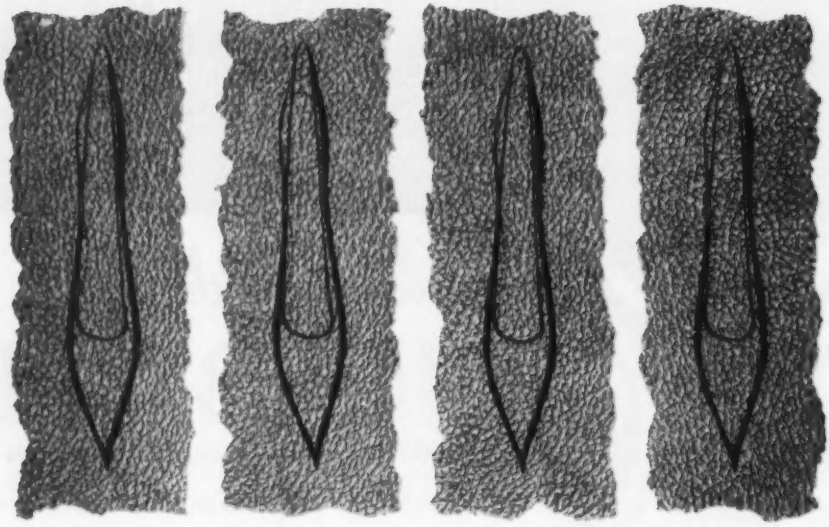

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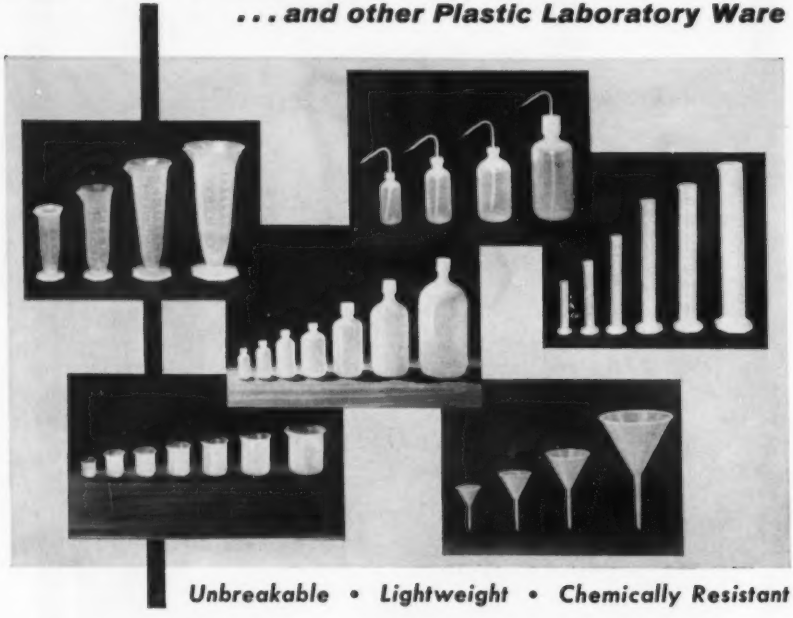

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Subscriptions—$12 per year for members; $15 for nonmembers.

DIMENSIONAL STABILITY OF IMPREGNATED SOLE LEATHER*

BERNARD H. FOUQUET

National Bureau of Standards

ABSTRACT

Sole leather impregnated with various polymeric substances shows less dimensional stability than finished vegetable-tanned leather. The application of pressure to sole leather increases both the density and the lateral dimensions. Maximum density and an increase in the rate of spreading are obtained with impregnated leather at a pressure of about 4000 psi. The dimensional stability of impregnated leather is improved by the use of hard resins in the impregnating formulations. To produce impregnated leather of optimum dimensional stability compression at a pressure of approximately 4000 psi should be used in the finishing operation.

—⋇—⋇—

INTRODUCTION

The effect of compression on the dimensional stability of sole leather has been given new significance by the steady development of new methods for upgrading leather by polymer impregnation. The use of polymers in place of inorganic salts as filling materials results in a leather with different physical properties.

The necessity for investigating the dimensional stability of impregnated leather was brought out in wear tests in which improperly rolled soles, impregnated with polyisobutylene, showed greater losses in thickness and more spreading (lateral expansion) than the regular vegetable-tanned soles used as controls. Since the apparent density of the leather increased greatly during wear, the lack of dimensional stability was considered to be due to the compression of the soles.

The lack of dimensional stability can be explained by the changes that take place in leather during the process of impregnation. Impregnation is carried out by immersing the leather in a solution of polymeric substances. The solution is absorbed by the leather matrix and fills the interstitial voids, during which time distention of the matrix takes place. During the drying process the solvent is evaporated out of the voids, leaving a coating of polymers on the fibers. Now the fibers are coated with a material which will

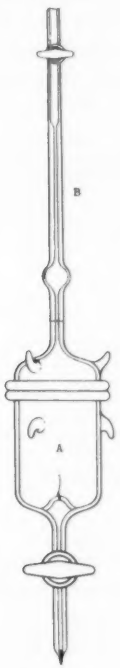
*This study was sponsored by the Bureau of Supplies and Accounts of the Department of the Navy as part of Research and Development Project NT 001-018.

permit them to slide over one another with more ease, so that when compression occurs, lateral expansion is induced to a greater extent than would normally take place in nonimpregnated leather. Some impregnants facilitate lateral expansion more than others, depending upon the viscoelastic properties of the polymeric materials used.

The changes in dimensions due to compression of the leather produce changes in the apparent density. The apparent or bulk density of a piece of leather may be calculated readily by an accurate determination of its bulk volume and weight, where:

$$\text{Apparent Density} = \frac{\text{Weight}}{\text{Area} \times \text{Thickness}}$$

At the initial stages of compression the decrease in thickness occurs at a greater rate than the increase in area; consequently, the density increases. However, when the fibers of impregnated leather have been compacted, the



Over-all Length: 21¼″

Inside Diameter of *A*: 2¼″

Height: 4½″

Bore of Capillary *B*: 3 mm.

FIGURE 1.—Volume measurement apparatus.

thickness decreases more gradually, and the change in area becomes greater; therefore, the density remains essentially constant.

TEST PROCEDURES

Apparent density.—The determination of the apparent density of the leather from worn impregnated soles was made on circular specimens two inches in diameter cut at the point where the maximum loss in thickness occurred. The specimens were cleaned of foreign particles by brushing and were conditioned at 70° ± 2°F. and 50 ± 2% relative humidity. The volumes of the specimens were determined by mercury displacement because of the nonuniformity in thickness of the worn soles. A diagram of this apparatus is shown in Fig. 1. *A* is the vessel in which the specimen is anchored by means of a platinum wire. This vessel is fitted with a cap from which extends a capillary tube *B*. The capillary at the bottom of the vessel is immersed in a bath of mercury under conditions of constant temperature and humidity. The apparatus is calibrated by filling it with mercury to the mark on the capillary *B* with the aid of suction from a vacuum pump. The mercury is than allowed to flow into a clean dry beaker. The leather specimen is attached to the platimum wire, and the mercury is drawn back into the vessel to the mark *B*. The mercury remaining in the beaker represents the volume displacement caused by the specimen under test. The mercury is then weighed, and the volume of the specimen is calculated.

The apparent densities of the other leather specimens used in this study were calculated from dimensional measurements. Specimens of leathers to be compressed were cut to a size of 2″ x 2″ by means of a steel die, and the irregularities of the edges caused by the die were removed by buffing. After conditioning for 24 hr. at 70° ± 2°F. and 50 ± 2% relative humidity, the dimensions along the edges were measured to within ±0.05 mm. with a cathetometer, and the thickness was determined to ±0.001″ at five clearly marked points at the corners and at the center. The weights of the specimens were recorded to the nearest mg.

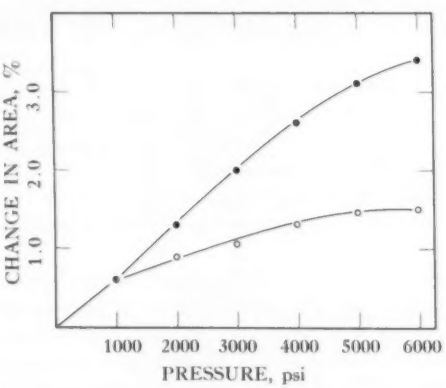


FIGURE 2.—Pressure-area curves obtained by two different methods. ○ using different specimens for each measurement; ● using the same specimen through the entire range of pressures.

Compression.—Two procedures for investigating the rate of change in area were studied. In one procedure the same specimen was subjected to pressures of 1000, 2000, 3000, 4000, 5000, and 6000 psi for a duration of 3 min., and the new dimensions were measured after each 1000 lb. increase in pressure. In the second procedure separate specimens were used for each 1000 psi per 3 min. increase in pressure. Figure 2 gives the change in area curves obtained by the two methods for nonimpregnated vegetable-tanned leather. The specimens used through the entire range of pressures show a larger amount of spreading.

The effect of time during which the specimen is subjected to pressure was investigated as a possible explanation for the difference in spreading obtained between the two methods. However, subjecting each finished vegetable-tanned leather specimen to a pressure of 6000 psi for time durations up to 18 min. gave no appreciable difference from the change in area of 1.5% obtained by a 3-min. compression. Results obtained by a similar method for impregnated leather, given in Table I, indicate that the time of application

TABLE I

EFFECT OF TIME ON THE CHANGE IN AREA DURING COMPRESSION OF SEPARATE SPECIMENS OF BUTYL-IMPREGNATED LEATHER*

Pressure, psi	Time, min.	Change in Area, %
6000	3	4.7
"	6	5.3
"	12	6.4
"	18	6.9

*With the same specimen being used for the entire range of pressure, this leather exhibited an increase in area of 8%, as shown in Fig. 5.

of pressure to each specimen affects the amount of spread. The increase in lateral expansion, however, is not equivalent to the amount obtained by using the same specimen through the six 3-min. stages in which the pressure is increased stepwise to 6000 psi.

The first procedure in which the same specimen is used through the entire range of pressures was adopted for the rest of this investigation.

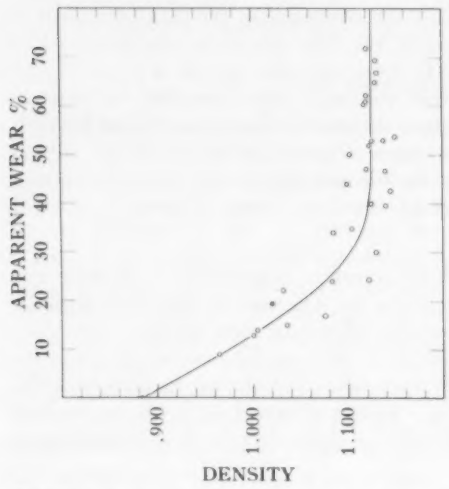


FIGURE 3.—Increase in density with apparent wear of polyisobutylene-impregnated leather soles.

RESULTS AND DISCUSSION

The increase in apparent density of a group of worn experimental polyisobutylene-impregnated soles which were not rolled, with the apparent percentage wear, is shown in Fig. 3. The apparent wear is a combination of the loss in thickness by abrasion and compression during wear. The density reaches a miximum value at a loss in thickness of 30 to 40%. An increase in area was observed for the worn soles; however, it was not possible to make accurate measurements of these changes.

Figure 4 shows the relation of density to percentage loss in thickness (percentage compression) with increase in pressure of the same stock polyisobutylene-impregnated leather that was used in the wear tests and for nonimpregnated vegetable-tanned sole leather. The impregnated leather reaches a maximum density at about 30% compression, approximately the same as that of the worn sole leather. The regular sole leather reaches a higher density under pressure which, however, does not become constant in the range of pressures used.

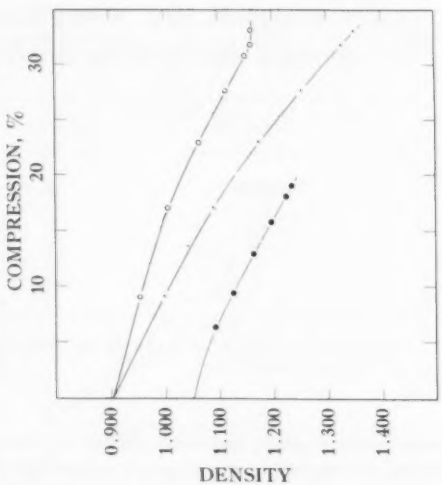


FIGURE 4.—Changes in density with compression. ○ polyisobutylene-impregnated leather; ● finished vegetable-tanned leather. (X curve represents the increase in density with compression computed assuming no increase in area for polyisobutylene-impregnated leather.)

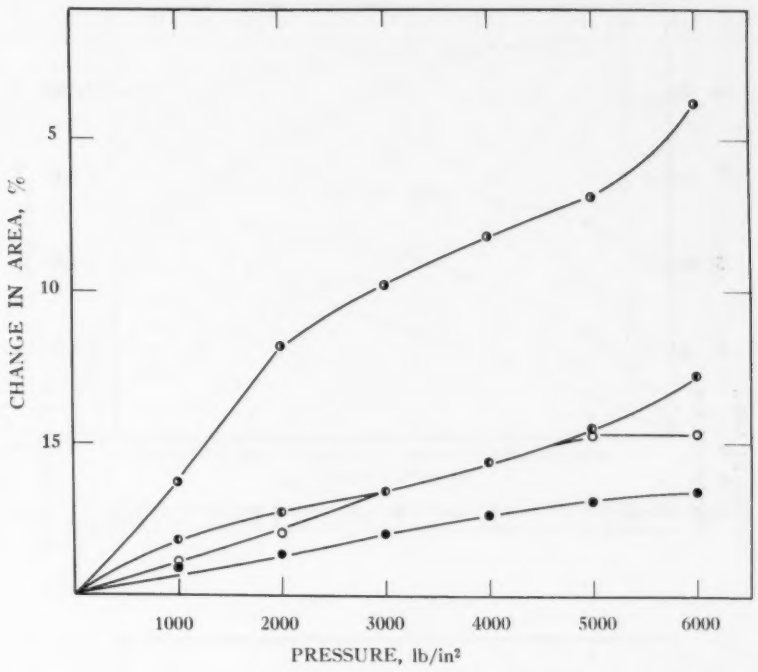


FIGURE 5.—Changes in area with compression. ◑ polyisobutylene-impregnated leather; ◐ commercial Butyl-impregnated leather; ● finished vegetable-tanned leather; 0 crust leather.

Figure 5 represents the curves for the change in area, with pressure for polyisobutylene-impregnated leather of the same stock as that used in the wear test, a commercial Butyl-impregnated sole leather which had been subjected to tannery rolling and finishing, ordinary sole leather, and vegetable-tanned natural crust leather. The values for the change in area are given as the percentage increase in area (Δ area $\times$ 100/original area).

Ordinary sole leather and crust leather show very little lateral expansion. Ordinary sole leather, however, is more stable because of the more compact fiber structure produced by rolling. The polyisobutylene-impregnated leather shows a considerable increase in spreading over the entire range of pressures. The Butyl-impregnated leather prepared and finished by tannery

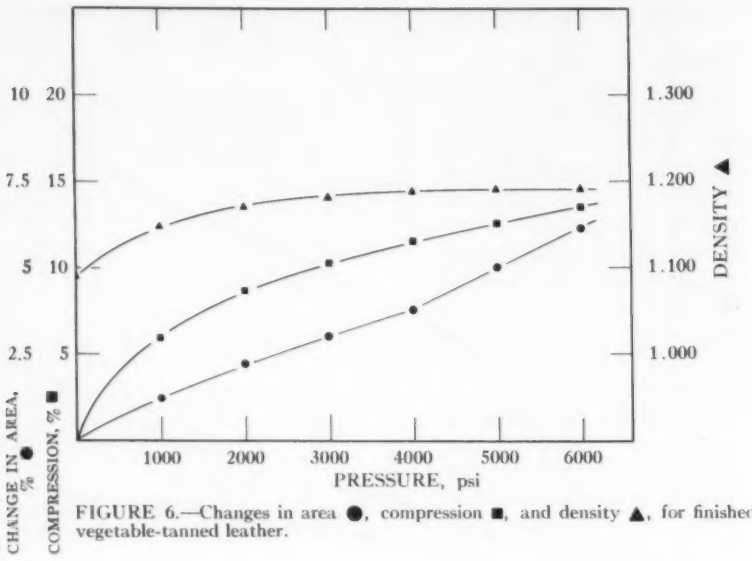


FIGURE 6.—Changes in area ●, compression ■, and density ▲, for finished vegetable-tanned leather.

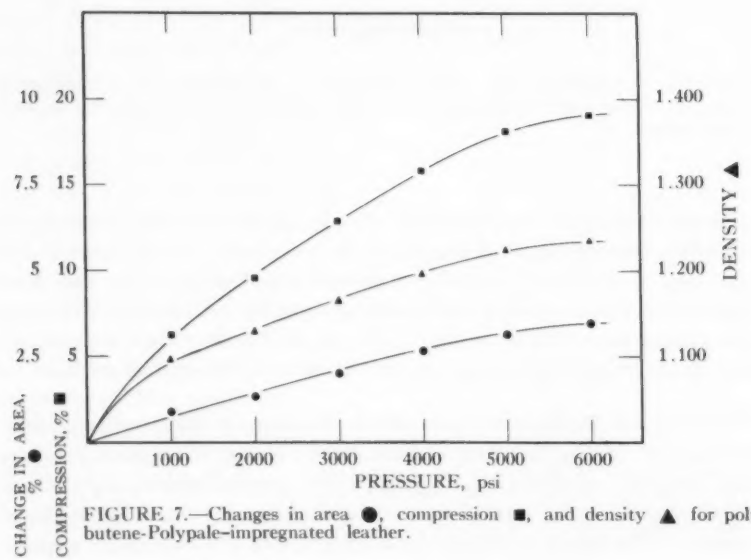


FIGURE 7.—Changes in area ●, compression ■, and density ▲ for polybutene-Polypale–impregnated leather.

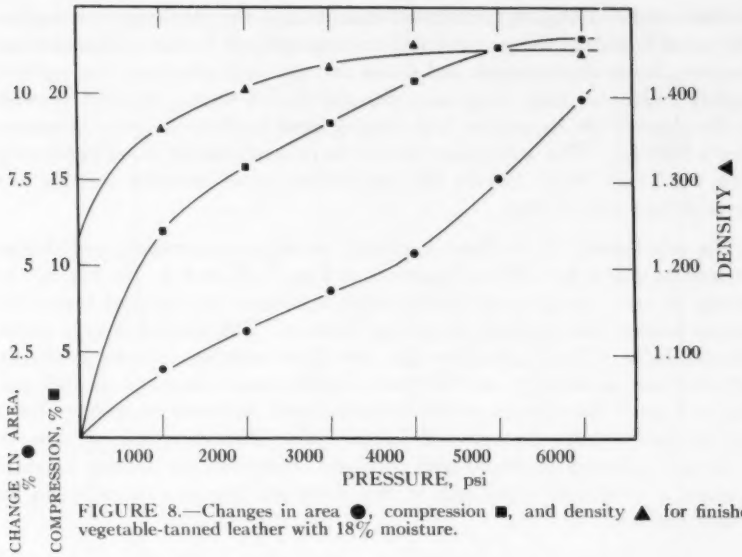


FIGURE 8.—Changes in area ●, compression ■, and density ▲ for finished vegetable-tanned leather with 18% moisture.

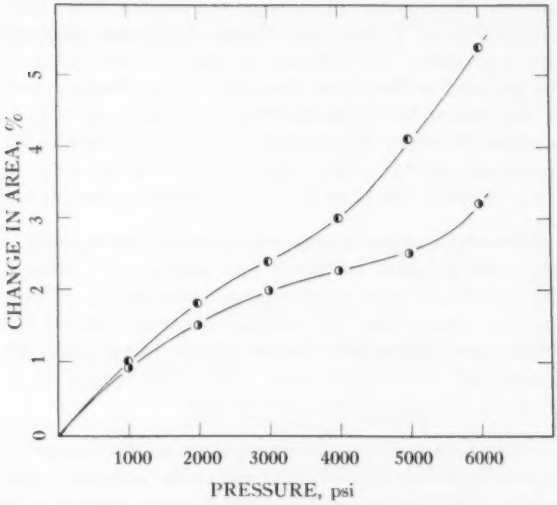


FIGURE 9.—Changes in area due to compression of polybutene-Polypale–impregnated leather ◐, and Vinsol-castor oil–impregnated leather ◑.

methods shows a slightly greater increase in area than ordinary sole leather but much less than the polyisobutylene-impregnated leather. This increase however, is not objectionable and shows that properly processed impregnated leather cannot undergo large area changes during wear. A rapid increase in the slope of the curves for both impregnated leathers occurs at pressures above 5000 psi. This is the point where the polymer-coated fibers apparently slide over each other, forcing the leather to spread laterally without any great change in thickness.

The relationship of the three variables, density, compression, and change in area, is shown for different leathers in Figs. 6, 7, and 8. In Fig. 6, the change in area, compression, and density are shown for finished vegetable-tanned leather with increase in applied pressure. This leather is very stable dimensionally. The graphs show that the three variables increase gradually with increase in pressure, and the rate of compression decreases at 5000 psi. Figure 7 gives the changes in the variables with increases in pressure for a polybutene-Polypale–impregnated leather (1). The compression (loss in thickness) increases gradually with pressure. However, the density becomes constant at about 4000 psi, and at this point the change in area shows an abrupt increase.

Since the change in area due to increased slipping of the fibers is believed to be caused by the lubrication effect of the impregnant, a test was made with regular finished sole leather to which 18% moisture was added. The moisture was added to provide lubrication between the fibers. The results for these tests are given in Fig. 8. Compression (loss in thickness) increased gradually with increase in pressure. The density reaches a maximum at a pressure of 3000 to 4000 psi, and at this point the rate of area change shows an abrupt increase. It may therefore be assumed that at the first application of pressure the viscous materials within the leather matrix redistribute to fill the pores, giving a maximum density. On further application of pressure these materials act as a lubricant between the fibers facilitating lateral expansion.

Figure 9 shows the changes in area with pressure for vegetable-tanned sole leather with water solubles extracted and impregnated with polybutene-Polypale and with Vinsol resin plasticized in castor oil (1). These specimens were all prepared from rolled and finished vegetable-tanned leather. The polybutene-Polypale–impregnated leather shows more spreading than the leather impregnated with Vinsol resin. Thus, the spread of impregnated leather depends on the type of impregnant used.

The effect of the different types of impregnants on the dimensional stability was investigated with leather impregnated with different ratios of polybutene-Polypale. This blend contains a low viscosity elastomer (polybutene) and a hard brittle resin (Polypale).

Figure 10 gives the change in lateral expansion due to the variations in the concentrations of polybutene and Polypale in the blend. Each point

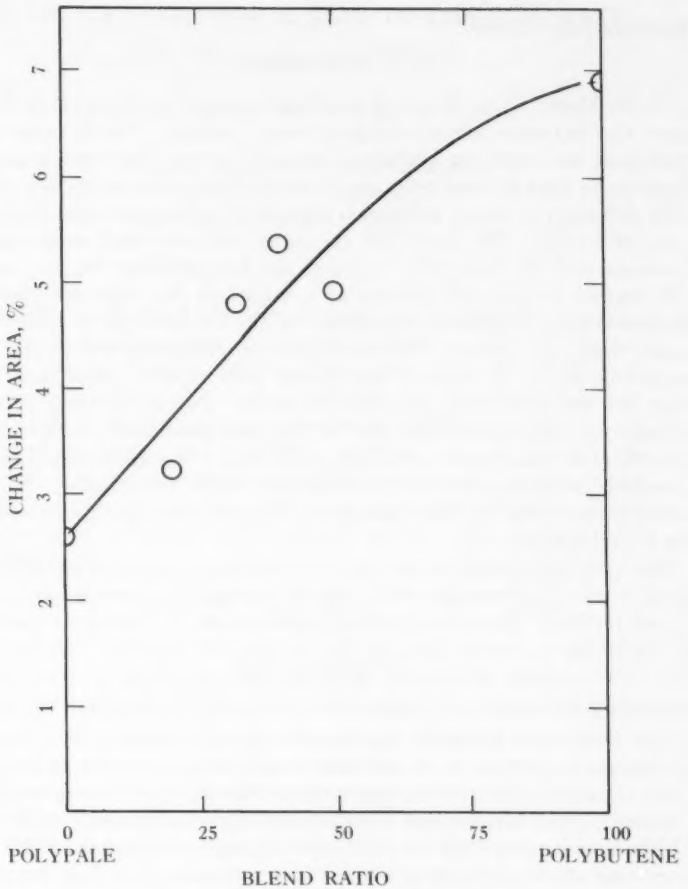


FIGURE 10.—Effect of ratio of elastomer to resin in impregnant on dimensional stability of impregnated leather.

represents the change in area obtained at 6000 psi. The change in area shows a definite increase with increasing polybutene concentration. This increase along with the values reported in Fig. 9 indicates how impregnation with elastomers results in dimensionally less stable leathers than impregnation with the harder resinous materials.

REFERENCE

1. Fouquet, B. H., and J. R. Kanagy. *JALCA*, **53**, 336, (1958).

Received July 6, 1959.

DISCUSSION

C. W. MANN (Q.M. Research and Engineering Center): I think Mr. Fouquet is to be congratulated on a good research study. This is a type of work that does not seem too glamorous to many people, but preliminary work needs to be done to correct for any faults that may show up on new products. This deficiency of lateral stability is not unique in this particular impregnated type of leather. We have had the same difficulty with some substitute tannages that we have tried. One of the first problems we ran into with sole leather tanned with Orotan as a substitute for vegetable tannin was decreased lateral stability—a tendency of the Orotan soles to spread a little faster than their mates. We found that the difference was in the rate of spreading and not in degree; the Orotan soles merely spread more rapidly than the standard vegetable-tanned mates. During the first few weeks of wear you might notice that one of your shoe soles was a little wider than the other, or would tend to curl up at the edge. But after six weeks or two months of wear, the other sole would spread to the same degree. It is interesting to note that by these measurements you have a good explanation for the lateral stability.

One question I would like to ask is whether or not we could use a technique along this line to determine what type of impregnation process has been used in sole leather? There is a growing interest now in impregnated soles, and we are trying to control their quality by chemical methods. We do not feel that these methods are entirely adequate, and accordingly any physical test that might tend to throw further light on that would be extremely valuable.

MR. FOUQUET: There are two answers to your question, Mr. Mann. If the leather were tested in its unrolled state, I think there would be a possibility of telling whether the impregnated material had been a resin or an elastomer type, becuase the elastomer-impregnated leather would spread a little more rapidly than the resin-type-impregnated leather would. However, most of these leathers are rolled after treatment, and I do not think it would be possible to tell once the leather has been rolled.

C. W. MANN: I was interested in the change in density that occurred in these leathers. The density of the soles tended to go up to 1.13 which corresponded to a relatively low pressure in the laboratory tests. From this it might be concluded that the amount of spreading under high pressure such as 6,000 pounds might be slightly misleading as indicating a fault in the leather. It may be that 6,000 pounds pressure is rather drastic and that you might expect some breaking apart of the fibers under those conditions.

THE USE OF FISH OILS FOR FATLIQUORING LEATHER

II. USE OF PHOSPHORIC ACID TO CONTROL RATE OF FISH OIL SULFATION

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ABSTRACT

Highly unsaturated oils such as menhaden are difficult to sulfate by conventional methods. In the present study on sulfation of ocean perch, herring, salmon, and menhaden oils, it was found that (*a*) dilution of sulfuric acid with phosphoric acid permitted close control of the rates of temperature rise and of sulfation and that (*b*) the ratio of phosphoric acid to sulfuric acid was a significant variable. By means of the phosphoric acid sulfating technique, a sulfated menhaden oil was prepared on a pilot-plant scale with properties similar to those of a commercially sulfated cod oil used in the leather industry.

—×—×—

INTRODUCTION

The U. S. Fish and Wildlife Service is interested in finding uses for menhaden oil in the leather industry. The raw oil, however, has a tendency to oxidize and to polymerize, and these properties do not favor its employment for such usages. Since sulfation would reduce this tendency, it was thought that a sulfated oil might be more suitable. Experts in the leather industry agreed that such a product would be desirable, but they pointed out that the same properties which make raw menhaden oil somewhat unsuitable for use in the manufacture of leather likewise make it difficult to sulfate.

The Fish and Wildlife Service also is interested in finding uses in leather processing for other fish oils such as those from ocean perch, herring, and salmon. In the present work, however, the primary interest was in menhaden oil, since it is available in largest quantity.

*Now associated with Rohm & Haas Company.

†The research reported in this paper was conducted by Tanners' Council Laboratory, University of Cincinnati, under a contract with the U. S. Fish and Wildlife Service. It was financed with funds available under provisions of Public Law 466, 83rd Congress, approved July 1, 1954, generally termed the Saltonstall-Kennedy Act.

A communication from T. M. Miller of Wallace Menhaden Products, Morehead City, North Carolina, indicated that phosphoric acid mixed with menhaden fish meal decreases the product's susceptibility to oxidation. In parallel agreement with this observation on meal, we noted in the laboratory that when concentrated phosphoric acid was added to menhaden oil, there was no appreciable rise in temperature. In further agreement with these findings, U. S. patent 2,243,991, which covers the use of phosphoric acid in sulfating olefins, claims that polymer formation is lessened.

Phosphoric acid is a strong synergist or metal scavenger, which inactivates pro-oxidants in the oil. Further, we observed a huge difference in the oxidation of menhaden oil, for example, when using dichromate dissolved in concentrated sulfuric acid as compared to dichromate dissolved in concentrated phosphoric acid. In the latter case, the oil was oxidized with no darkening or noticeable polymerization. In one experiment, the addition of dichromate-phosphoric acid produced no oxidation until the temperature of the reaction was raised above 20° C. This observation would indicate that, depending upon the amount of phosphoric acid used with sulfuric acid in sulfating an oil such as menhaden, the amount of charring or burning of the oil can be reduced. This fact would be true regardless of how the phosphoric acid influenced the oxidation and sulfation reactions when mixed with sulfuric acid in sulfating an oil.

It therefore was believed that by mixing the highly reactive sulfuric acid with the less reactive phosphoric acid in sulfating menhaden oil, the temperature of the reaction, as well as the rate of oxidation and sulfation, might be reduced. It further was assumed that this effect might vary according to the proportion of phosphoric acid and sulfuric acid used. If these hypotheses were found to be true, phosphoric acid could be employed to control the sulfation of menhaden oil, thereby reducing the danger of excessive oxidation and polymerization that occurs when this oil is sulfated with sulfuric acid alone.

The work reported here accordingly was divided into three phases, with the following objectives:

1. To determine if phosphoric acid could be used to decrease the temperature and the extent of sulfation and oxidation reactions occurring with an oil.
2. To study the effect of varying the ratio of phosphoric acid to sulfuric acid.
3. To test the laboratory findings on a pilot-plant scale (2).

EFFECT OF PHOSPHORIC ACID ON TEMPERATURE AND RATE OF SULFATION

The addition of water to concentrated sulfuric acid in sulfating an oil can reduce the temperature of the reaction. If 85% phosphoric acid were mixed

with concentrated sulfuric acid, the effect of phosphoric acid in controlling the sulfation reaction would be confounded by the water present.

Since water is known to be an important factor, an experiment therefore was set up to test the effect on temperature of sulfation of phosphoric acid under both anhydrous and hydrous conditions.

Experimental.—Samples of menhaden weighing 100 g. were cooled to about 20°C. Then, while being stirred at 160 rpm, the following acids and acid mixtures were added in 3 minutes, during which time and subsequently to it the temperature was recorded every minute for a total time of 10 minutes:

1. Acids added under anhydrous conditions

   a. 19 g. of 100% sulfuric acid (prepared by mixing appropriate quantities of 95% sulfuric acid with fuming sulfuric acid)

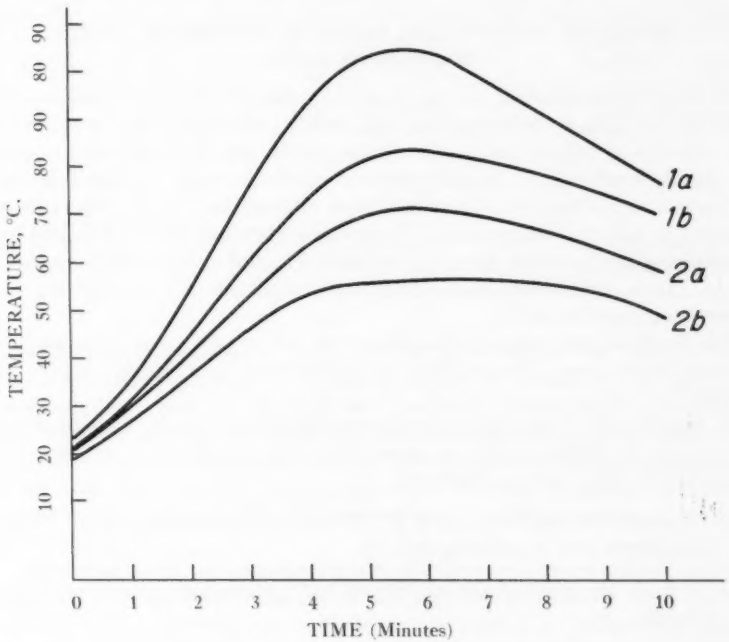

FIGURE 1.—Effect on temperature of sulfation of including phosphoric acid, under both anhydrous and hydrous conditions. The curves give the effect of adding to 100 g. of menhaden oil the following: (1a) 19 g. of 100% sulfuric acid; (1b) 10 g. of polyphosphoric acid + 20 g. of 95% sulfuric acid; (2a) 20 g. of 95% sulfuric acid; and (2b) 3 g. of 100% phosphoric acid + 20 g. of 95% sulfuric acid.

b. 20 g. of 95% sulfuric acid mixed with 10 g. of polyphosphoric acid of ortho equivalent of 115%

2. Acids added under hydrous conditions

a. 20 g. of 95% sulfuric acid
b. 20 g. of 95% sulfuric acid mixed with 3 g. of 100% phosphoric acid (prepared by mixing equal weights of 85% phosphoric acid with polyphosphoric atid of ortho equivalent of 115%)

In the above four acid systems, the SO_3 contents are equivalent.

Results.—The data given in Fig. 1 show that phosphoric acid under both anhydrous and hydrous conditions decreases the temperature of the sulfation reaction. They also show that, as was anticipated, the temperature of the reaction is lower if water is present.

EFFECT OF VARYING THE RATIO OF PHOSPHORIC ACID TO SULFURIC ACID

In the sulfation of an oil, the reactions that can occur may be classified into three groups: (A) hydrolysis of the triglyceride ester to give free fatty acids, (B) addition of sulfuric acid to the double bonds, and (C) other reactions at the double bonds caused by oxidation and polymerization. It therefore was of interest to see how these reactions were affected by varying the ratio of phosphoric acid to sulfuric acid. These three reactions can be followed by determining acid number, percent combined SO_3, and iodine number, respectively. It is understood that iodine numbers do not differentiate the reactions in groups B and C.

The fundamental purpose of sulfating an oil is, of course, to render it miscible with water. Its stability as an emulsion, accordingly, also is of interest.

To test the effect on these several properties of varying the ratio of phosphoric acid to sulfuric acid, we performed three experiments, the specific objectives of which were as follows:

1. To study the effect of adding 3% (weight acid to weight oil) of 100% phosphoric acid in sulfating fish oil.

2. To study the effect of adding 10% of 100% phosphoric acid in sulfating fish oils.

3. To study the effect of adding 5% of polyphosphoric acid in sulfating fish oils.

An example of the statistical design used for sulfation experiments I, II, and III is given in Table I for sulfation experiment I. Under process the

acid conditions to be compared within an experiment are given. Oil number indicates the number assigned to the four fish oils to be sulfated. The replicate letters indicate that each fish oil was sulfated twice using the same process. In Table I there are two identical oil samples for each oil number, and each of these oil samples was sulfated at the same time using identical conditions except for differences in acid conditions.

TABLE I

EXPERIMENTAL DESIGN IN SULFATING FISH OILS

Experiment I

Replicates	Oil No.	Process 1	Process 2
		3% of 100% H_3PO_4 + 20% of Conc. H_2SO_4 on Oil Weight Basis	10% of 100% H_3PO_4 + 20% of Conc. H_2SO_4 on Oil Weight Basis
1	1	Salmon Oil	Salmon Oil
	2	Perch Oil	Perch Oil
	3	Herring Oil	Herring Oil
	4	Menhaden Oil	Menhaden Oil
2	1	Salmon Oil	Salmon Oil
	2	Perch Oil	Perch Oil
	3	Herring Oil	Herring Oil
	4	Menhaden Oil	Menhaden Oil

Sulfation Experiment I (*3% of 100% phosphoric acid added*)—The experiment was of split-plot statistical design (1) made for the principal purpose of determining differences between acid systems as they affect total acid number, percent combined SO_3, and iodine number. This design was selected because by sulfating, washing, and neutralizing simultaneously and identically, variations in time and procedure virtually could be eliminated, which would make possible a better estimate of differences due to the acid system used.

One ocean perch oil, two herring oils of different iodine numbers, one salmon oil, and two menhaden oils of different iodine numbers were the oils sulfated. The following gives the procedure used in sulfating them and in analyzing them for total acid number, percent combined SO_3, iodine number, emulsion stability, and polymerization properties. The analyses for total acid number, percent combined SO_3, and iodine number were run in duplicate. The sulfation procedure for each oil was replicated and is referred to as replicate 1 and replicate 2.

Sulfation process.—Two sulfation processes were used. Process 1 was as follows:

1. Add 40 g. of 95% sulfuric acid to 200 g. of fish oil in 30 minutes, while maintaining the temperature of reaction between 15° and 20° C. and stirring at 160 rpm.
2. After the acid has been added completely, continue the reaction at this same temperature and rate of stirring for an additional 30 minutes.
3. While continuing the stirring, add 400 ml. of 15% sodium sulfate solution in 3 minutes and separate water layer at end of 4 hours.
4. Wash again with 400 ml. of 10% sodium sulfate solution. Remove the water layer at the end of 20 hours.
5. Neutralize to a pH of about 6 with 30% sodium hydroxide.

Process 2 was the same as process 1 except that a mixture of 40 g. of 95% sulfuric acid plus 6 g. of 100% phosphoric acid was used instead of 40 g. of 95% sulfuric acid alone.

Analysis for total acid number.—Acid numbers were determined on the neutralized sulfated oils substantially according to the procedure of the American Leather Chemists' Association (3). The procedure was modified, however, so as to determine the total acid number. This modification was accomplished by titrating a sample of sulfated oil to an alkaline pH with phenolphthalein and then back titrating to a faintly pink methyl orange end point with acid. The amount of acid required to titrate the sample then was corrected to total acid number units.

Analysis for percent combined SO_3.—The analyses for SO_3 were carried out according to the standard procedure of the American Leather Chemists Association (3).

Analysis for iodine number.—The sample of sulfated oil for determination of iodine number was taken prior to neutralization. The oil sample was dissolved in ether and washed free of acid with saturated salt water. Twenty-five ml. of the ether layer containing the dissolved sulfated oil was placed in a 100-ml. beaker, and the ether was evaporated off on a steam bath. This sample then was used for determining iodine number by means of the Hanus procedure.

Analysis for emulsion stability.—The test for stability of emulsion consisted in emulsifying 10 g. of sulfated oil with 100 ml. of water. If the oil did not break from the emulsion before 2 hours, the oil emulsion was considered sufficiently stable for use in fatliquoring leather.

Analysis for polymerization.—A 3-g. sample was weighed in a 100-ml. beaker and placed in a forced-air oven for 24 hours at 100° C. The purpose of the test was to determine if the sulfated products would form a hard film and consequently produce undesirable effects on leather.

TABLE II

SULFATION EXPERIMENT I

EFFECT OF ADDING 3% OF 100% PHOSPHORIC ACID IN SULFATING FISH OIL

RAW OIL		SULFATED OIL									
			Total Acid Number			Percent Combined SO_3			Iodine Number		
Kind	Iodine Number	Process	Replicate 1	Replicate 2	Avg.	Replicate 1	Replicate 2	Avg.	Replicate 1	Replicate 2	Avg.
Perch	119	1	53.29	56.78	55.04	6.30	6.33	6.32	81	79	80
oil	119	2	43.19	58.32	50.76	5.78	5.85	5.82	85	81	83
Herring	131	1	53.09	47.54	50.32	5.93	5.82	5.88	88	87	88
oil	131	2	51.31	48.57	49.94	5.75	5.77	5.76	89	93	91
Herring	139	1	45.23	37.81	41.52	5.85	6.05	5.95	96	97	96
oil	139	2	41.54	46.41	43.98	5.42	5.38	5.40	97	98	98
Salmon	166	1	42.22	41.95	42.08	5.79	5.57	5.68	119	118	118
oil	166	2	40.76	48.27	44.52	5.32	5.05	5.18	123	125	124
Menhaden	152	1	42.12	40.15	41.14	5.59	4.94	5.26	106	114	110
oil	152	2	34.68	34.86	34.77	5.24	4.09	4.66	114	120	117
Menhaden	176	1	39.66	34.17	36.92	4.48	4.60	4.54	134	138	136
oil	176	2	38.17	40.95	39.56	4.63	4.00	4.32	139	143	141
Mean		1			44.50			5.60			104.7
value		2			43.92			5.19			108.7

Process 1—200 g. of fish oil was sulfated with 40 g. of 95% sulfuric acid.
Process 2—200 g. of fish oil was sulfated with a mixture of 40 g. of 95% sulfuric acid + 6 g. of 100% phosphoric acid.

TABLE III

SULFATION EXPERIMENT II

EFFECT OF ADDING 10% OF 100% PHOSPHORIC ACID IN SULFATING FISH OIL

RAW OIL		SULFATED OIL									
			Total Acid Number			Percent Combined SO_3			Iodine Number		
Kind	Iodine Number	Process	Replicate 1	Replicate 2	Avg.	Replicate 1	Replicate 2	Avg.	Replicate 1	Replicate 2	Avg.
Perch	119	2	58.09	74.44	66.26	5.43	5.13	5.28	88	85	86
oil	119	3	61.09	83.03	72.06	4.20	4.20	4.20	98	100	99
Herring	131	2	47.75	56.22	51.98	5.04	4.34	4.69	93	93	93
oil	131	3	60.29	64.52	62.40	4.37	3.54	3.96	98	107	102
Salmon	166	2	41.63	56.70	49.16	4.87	4.77	4.82	123	126	124
oil	166	3	47.97	63.96	55.96	4.24	4.04	4.14	133	137	135
Menhaden	176	2	34.57	39.90	37.24	5.09	4.55	4.82	139	146	142
	176	3	40.08	53.99	47.04	4.20	3.96	4.08	150	157	154
Mean		2			51.16			4.90			111.3
value		3			59.37			4.10			122.5

Process 2—200 g. of fish oil was sulfated with a mixture of 40 g. of 95% sulfuric acid + 6 g. of 100% phosphoric acid.
Process 3—200 g. of fish oil was sulfated with a mixture of 40 g. of 95% sulfuric acid. + 20 g. of 100% phosphoric acid.

TABLE IV

SULFATION EXPERIMENT III

EFFECT OF ADDING 5% OF 100% PHOSPHORIC ACID IN SULFATING FISH OIL

RAW OIL		SULFATED OIL									
			Total Acid Number			Percent Combined SO_3			Iodine Number		
Kind	Iodine Number	Process	Replicate 1	Replicate 2	Avg.	Replicate 1	Replicate 2	Avg.	Replicate 1	Replicate 2	Avg.
Perch	119	1	71.29	53.56	62.42	5.31	5.38	5.34	88	86	87
oil	119	4	77.14	66.96	72.05	5.70	5.69	5.70	87	83	85
Herring	131	1	68.90	54.92	61.91	5.10	5.40	5.25	92	92	92
oil	131	4	80.95	65.92	73.44	6.41	5.74	6.08	88	88	88
Salmon	166	1	51.71	58.92	55.32	5.18	5.32	5.25	125	122	124
oil	166	4	55.67	62.35	59.01	5.58	5.80	5.69	122	118	120
Menhaden	176	1	42.07	37.10	39.58	4.94	4.78	4.86	149	144	142
oil	176	4	48.69	41.54	45.12	5.54	5.38	5.46	139	141	140
Mean		1			54.81			5.18			111.1
value		4			62.40			5.73			108.2

Process 1—200 g. of fish oil was sulfated with 40 g. of 95% sulfuric acid.
Process 4—200 g. of fish oil was sulfated with a mixture of 40 g. of 95% sulfuric acid + 10 g. of polyphosphoric acid.

Results.—The results of sulfation experiment I are given in Table II. An analysis of variance indicated that there were significant differences in iodine number and percent combined SO_3 between processes 1 and 2. The mean values at the bottom of Table I indicate that when 3% of 100% phosphoric acid (process 2) was used, the SO_3 content was lower and the iodine number was higher than when phosphoric acid was not used (process 1).

The emulsion stability and polymerization properties were good, as was found to be the case also for all the oils observed in the present study. When, as an experiment, these oils were deliberately polymerized, they became jelly-like.

Sulfation Experiment II (*10% of 100% phosphoric acid added*)

Procedure.—The procedure used in sulfation experiment II was the same as that used in sulfation experiment I except that process 1 was replaced by process 3. In short, process 2 was compared with process 3 rather than with process 1. Process 3 differed from process 2 only in that a mixture of 40 g. of 95% sulfuric acid plus 20 g. of 100% phosphoric acid was used (instead of 40 g. of 95% sulfuric acid plus 6 g. of 100% phosphoric acid). The 20 g. of 100% phosphoric acid in process 3 is 10% of the weight of oil (200 g.) in thar process.

Results.—The data are given in Table III. An analysis of variance indicated significant differences between process 2 and 3 for total acid number, percent combined SO_3, and iodine number. The mean values given at the bottom of the table indicate that when 10% of 100% phosphoric acid was used (process 3), the total acid numbers and iodine numbers were higher, and the SO_3 content was lower. Increasing the amount of 100% phosphoric acid decreased the sum of oxidation and sulfation reactions occurring on the triglyceride and increased the hydrolysis of the ester.

Sulfation Experiment III (*5% of polyphosphoric acid added*)

Procedure.—The procedure used in sulfation experiment III was the same as that used in sulfation experiment I except that process 2 was replaced by process 4. In short, process 1 was compared with process 4 rather than with process 2. Process 4 differed from process 1 only in that a mixture of 40 g. of 95% sulfuric acid plus 10 g. of polyphosphoric acid of ortho equivalent of 115% was used (instead of 40 g. of 95% sulfuric acid containing no phosphoric acid). The 10 g. of polyphosphoric acid in process 4 is 5% of the weight of oil (200 g.) in that process.

Results.—The purpose of sulfation experiment III was to study the effect of decreasing the moisture content of sulfuric acid in sulfating an oil. The data are given in Table IV. An analysis of variance indicates significant differences between processes 1 and 4 for iodine number, percent combined

SO_3, and total acid number. Use of polyphosphoric acid increased the sum of the oxidation and sulfation reactions occurring on the triglycerides and increased the hydrolysis of the ester. The effect of polyphosphoric acid in controlling the sulfation reaction in this experiment cannot be determined because it is confounded with a decrease in water content. This experiment does indicate, however, that the use of polyphosphoric acid can increase the SO_3 content and may be of some advantage, in this respect, in replacing fuming sulfuric acid.

PILOT-PLANT STUDIES

The results of the laboratory experiments were encouraging. A pilot-plant sulfation study of menhaden oil therefore was undertaken at a cooperating private company engaged in the sulfation of oils. The pilot-plant study concerned only menhaden oil because, of the fish oils studied, it was one the most difficult to sulfate by regular methods.

Experimental.—The sulfation procedure used in the pilot-plant experiments was identical to that employed in sulfation experiment I. (The proportions thus were 200 parts of oil to 40 parts of 95% sulfuric acid mixed with 6 parts of 100% phosphoric acid—all by weight.) A commercially sulfated cod oil made in the regular way for the leather industry was used for comparison.

Results.—The following comments were made by the cooperating chemical company regarding the laboratory-developed procedure when it was applied in the pilot plant: "In attempting to follow the procedure as outlined in making sulfated menhaden oil 1, two batches were made, but in each instance a clear, stable product was not obtained that would have the proper degree of SO_3 content. On the third trial a slight modification was made in that the batch was neutralized after 1 hour in the wash in order that it would not remain acid and cause excessive hydrolysis, which seemed to be the cause of the failure of the first two batches. It was noted in the case of sulfated menhaden oil 2, which was brought up to an acid value equivalent to the commercially sulfated cod oil, that there was considerable stearine formation. From all indications the sulfated menhaden oil cannot be made with as high an acid value as regular cod oil. This might have a bearing on takeup, penetration, and distribution of the oil in the leather."

No mention was made that excessive oxidation and polymerization of menhaden oil had been reduced during sulfation with the phosphoric–sulfuric acid laboratory procedure. It therefore was assumed that this no longer was a problem, or the fact would have been made known. A comparison of the pilot-plant sulfated menhaden oil prepared using a phosphoric–sulfuric acid mixture with a product prepared by the cooperating company under a layer

of nitrogen and using concentrated sulfuric acid revealed that the phosphoric–sulfuric acid mixture produced a product lighter in color. This is another indication that the use of phosphoric acid with sulfuric acid in sulfating menhaden oil has reduced oxidation and polymerization of the oil.

TABLE V

COMPARISON OF ANALYTICAL DATA FOR A COMMERCIALLY SULFATED COD OIL WITH THAT OF TWO MENHADEN OILS SULFATED ON A PILOT-PLANT SCALE

Kind of Sulfated Oil	Acid Number	% Combined SO_3	Total Alkali	pH	% H_2O
Cod	41	4.7	1.3	6.50	25
Menhaden 1	13	5.6	0.52	6.20	25
Menhaden 2	46	4.7	1.2	6.25	25

Note: The menhaden oils were sulfated using a mixture of 200 parts of oil to 40 parts of 95% sulfuric acid plus 6 parts of 100% phosphoric acid—all by weight.

The data on the pilot-plant experiment are given in Table V. The analytical values for the cod oil show approximately the desired specifications of a sulfated fish oil for use in leather manufacture. The data thus indicate that by employing the phosphoric acid–sulfuric acid procedure developed in the laboratory, a sulfated menhaden oil was manufactured that met the desired specifications.

CONCLUSIONS

1. The assumption that the temperature of the reaction as well as the extent or rate of the oxidation and sulfation reactions occurring can be reduced by diluting highly reactive concentrated sulfuric acid with much less reactive phosphoric acid when sulfating an oil has been proven valid.

2a. Also confirmed was the fact that the reductions in temperature and rates of oxidation and sulfation vary according to the proportion of 100% phosphoric acid used. The higher the ratio of 100% phosphoric acid to 95% sulfuric acid, the greater is the reduction.

b. It also was found that an increase in the SO_3 content of an oil can be obtained by dehydrating concentrated sulfuric acid with polyphosphoric acid. Such a system could have advantages over that of using fuming sulfuric acid for sulfating oils. This postulate is based on the fact that the present time-temperature sulfation studies of fish oils indicated that a sulfuric acid system dehydrated with polyphosphoric acid and added to menhaden oil showed a lower temperature increase with time than did an anhydrous 100% sulfuric acid system added to the oil.

c. These studies showed that the sulfation reaction of a highly reactive oil, such as menhaden, can be controlled by the use of 100% phosphoric acid.

d. It also was found that the use of 100% phosphoric acid did not produce an undesirable sulfated product even when used in high proportions.

3. Pilot-plant experiments confirmed the laboratory findings and indicated that the phosphoric-sulfuric acid systems described in this paper produced acceptable sulfated products. They also indicated that this procedure successfully sulfated menhaden oil on a pilot-plant scale. Use of the phosphoric-sulfuric acid system for sulfating an oil would be advantageous, however, only in cases where the oil is difficult to sulfate by standard methods. This procedure was developed primarily for the sulfation of menhaden oil.

ACKNOWLEDGMENT

Grateful acknowledgment is given to NOPCO Chemical Company of Harrison, N. J. for their kind cooperation in the pilot-plant study.

REFERENCES

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Received December 18, 1958.

The early use of leather in armor is pointed up by these verses from the Iliad:

> Achilles threw in turn his ponderous spear
> And struck the circle of Aeneas' shield
> Near the first rim, where thinnest lay the brass
> And thinnest too the o'erlaying hide.

Some perfectly delightful verses on the uses of leather and praises thereof are contained in the book, *Leather in Life, Art and Industry* by John W. Waterer (London, 1946, Faber and Faber Limited), pp. 52 and 53, reprinted there with permission of the Rev. F. J. Dove and *Leather Guilds*.

Several interesting sections on the early uses of leather, prices of leather goods, historic opinions of the leather trades, and descriptions of tanneries are contained in the series, *Studies in Ancient Technology*, Vol. V, by R. J. Forbes, published by E. J. Brill in Leiden, the Netherlands, in 1957.

METHODS FOR INDUSTRIAL WASTE ANALYSIS*

PHYSICAL AND CHEMICAL EXAMINATION OF INDUSTRIAL WASTES (METHOD M1)

The procedures described herein are intended for use in the industrial waste field. Because of the wide variety of industrial wastes, all the procedures may not be applicable to a specific waste or combination of wastes. Hence, some modification of a procedure may be necessary in specific instances. Whenever a procedure is modified, the nature of such modification must be plainly stated in the report of results.

Collection of samples

Sampling and analyzing industrial wastes usually require greater care and attention to details than sampling and analyzing sewage and sewage effluents. Industrial wastes are subject to rapid changes even within a few minutes, due to breakdowns, spillovers, floor-washing, evaporator entrainment, and numerous causes which happen frequently even in the best operated plants.

The purpose of sampling and analyzing may be to show:

(*a*) the peak load concentration,

(*b*) the duration of peak loads,

(*c*) the occurrence of variation throughout the day.

(In these cases, samples should be taken often enough to show the desired results, i.e., every 5, 10, 15, or 60 min., and analyzed separately.)

(*d*) the average loss during a shift or a 24-hr. period.

In this case, the individual samples which are collected every few minutes or hourly should be composited in proportion to the flow, preserved, if necessary, and analyzed as soon as possible.

Preservation of samples

Preservation of samples is difficult because almost all preservatives interfere with some of the tests. Immediate analysis is ideal. Storage at low temperatures, 4°C., is perhaps best to preserve most samples until the next day. Chemical preservatives are to be used only when they are shown not to interfere with the examinations being made.

Expression of results

Results may be expressed as milligrams per liter, mg/l, or parts per million, ppm. However, where it is pertinent, the specific gravity, sp.g., shall be

*The Industrial Wastes Committee, with Past President E. B. Thorstensen as Chairman, has assembled these methods from *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes* (10th ed., 1955), issued by APHA—AWWA—FSIWA, and recommended their adoption by ALCA. Council has approved this and authorized their publication herewith as provisional ALCA methods.

given. If the concentration is less than 1 mg/l the results may be expressed as micrograms per liter, μg/l, or parts per billion, ppb, where billion is understood to be 10^9. If the concentration is greater than 10,000 mg/l the results should be expressed as percent, 1% being equivalent to 10,000 mg/l. In brines or wastes of high sp.g. a correction must be made for the sp.g. if the results are expressed as ppm or percent by weight. In such cases the sp.g. must be given with the data:

$$\text{ppm by weight} = \frac{\text{mg/l}}{\text{sp.g.}}$$

Reference: *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes.* Tenth edition, 1955. APHA-AWWA-FSIWA. p. 283.

OXYGEN (METHOD M2)

(DISSOLVED OXYGEN)

Collection of samples

Collect the sample in narrow-mouth glass-stoppered bottles of 250- to 300-ml. capacity. Special precautions are required to avoid entrainment or solution of atmospheric oxygen. In sampling from a line under pressure, a glass or rubber tube attached to the tap should extend to the bottom of the bottle. Allow the bottle to overflow 2 or 3 times its volume, and replace the stopper so that no air bubbles are entrained.

Samplers which permit collection of dissolved oxygen, BOD, and other samples from streams, ponds, or tanks of moderate depth are of the type shown in Fig. 1. Water from depth samples taken in a 1- to 3-liter Juday bottle is bled from the bottom through a tube extending to the bottom of a 250- to 300-ml. dissolved-oxygen bottle. In sampling from a reservoir at considerable depth a sampler provided with a valve release should be used. The temperature of the sampled water should be recorded to the nearest degree centigrade or more precisely as desired.

Preservation of samples

There should be no delay in the determination of dissolved oxygen on all samples that contain an appreciable iodine demand or ferric iron. Preservation of samples for 4 to 8 hr. is accomplished by adding 0.7 ml. conc. H_2SO_4 and 1 ml. of 2% sodium azide to the dissolved-oxygen bottle. This will arrest biological activity and maintain the dissolved oxygen if the bottle is stored

at the temperature of collection or water-sealed and kept at a temperature of 10° to 20°C. As soon as possible, complete the procedure using 2 ml. $MnSO_4$ solution, 4.0 ml. alkaline iodide solution, and 2 ml. conc. H_2SO_4.

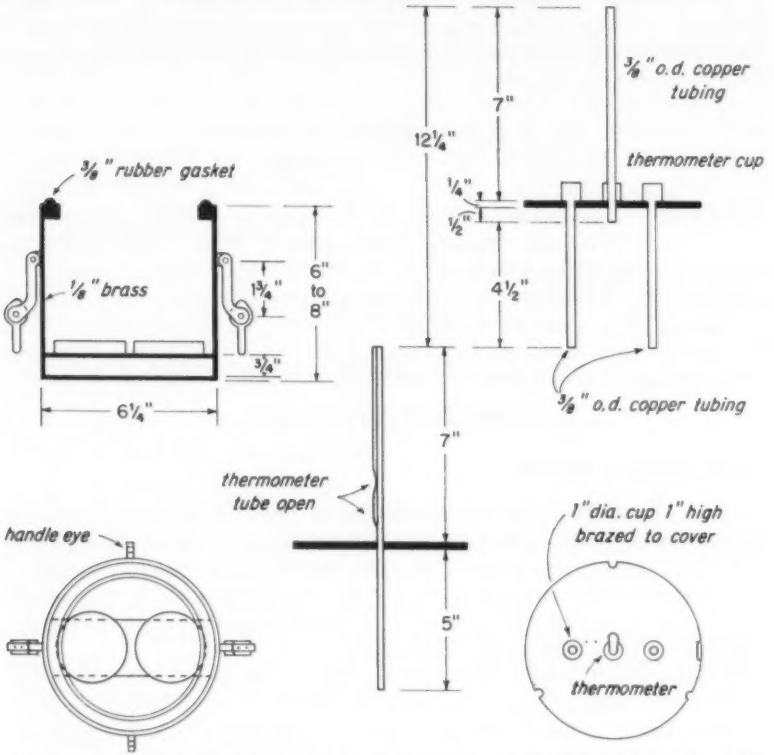

FIGURE 1.—Dissolved Oxygen and Biochemical Oxygen Demand Sampler Assembly.

Selection of method

The Alsterberg (sodium azide) modification will be used.

ALSTERBERG (AZIDE) MODIFICATION

1. General discussion

This modification is used for waters containing more than 0.1 mg/l nitrite N and not more than 1 mg/l ferrous Fe. Other reducing or oxidizing materials should be absent. If 1 ml. fluoride solution is added before acidifying

the sample and there is no delay in titration, the method is also applicable in the presence of 100 to 200 mg/l ferric Fe.

2. Reagents

2.1. *Manganous sulfate solution.* Dissolve 480 g. $MnSO_4 \cdot 4H_2O$ or 400 g. $MnSO_4 \cdot 2H_2O$ or 364 g. $MnSO_4 \cdot H_2O$ in distilled water, filter, and dilute to 1 liter. When uncertainty exists regarding the water of crystallization, a solution of equivalent strength may be obtained by adjusting the specific gravity of the solution to a value of 1.270 at 20°C. The manganous sulfate solution should liberate not more than a trace of iodine when added to an acidified solution of potassium iodide.

2.2. *Alkaline-iodide reagent.* Dissolve 500 g. NaOH or 700 g. KOH, and 135 g. NaI, or 150 g. KI, in distilled water, and dilute to 1 liter. Potassium and sodium salts may be used interchangeably. The reagent should not give a color with starch solution when diluted and acidified.

2.3. *Sulfuric acid, concentrated.* The strength of this acid is about 36*N*. Hence, 1 ml. is equivalent to about 3 ml. of the alkaline-iodide reagent.

2.4. *Starch solution.* An emulsion of 5 to 6 g. potato, arrowroot, or soluble starch is made in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few min., and let settle overnight. Use the clear supernatant. This solution may be preserved with 1.25 g. salicylic acid per liter or by the addition of a few drops of toluene.

2.5. *Standard potassium bi-iodate solution.* A stock solution equivalent in strength to 0.1*N* thiosulfate solution contains 3.250 g. $KIO_3 \cdot HIO_3$ per liter in accordance with the following reaction:

$$2\ KIO_3 \cdot HIO_3 + 20\ KI + 11\ H_2SO_4 = 11\ K_2SO_4 + 12\ H_2O + 12\ I_2$$

The bi-iodate solution equivalent to the 0.025*N* thiosulfate contains 0.8124 g. $KIO_3 \cdot HIO_3$ per liter and may be prepared by diluting 250 ml. stock solution to 1 liter.

2.6. *Standard potassium dichromate solution.* $K_2Cr_2O_7$ may be substituted for $KIO_3 \cdot HIO_3$. A solution equivalent to 0.025*N* sodium thiosulfate contains 1.226 g. $K_2Cr_2O_7$ per liter. The $K_2Cr_2O_7$ should be previously dried at 103° C. for 2 hr.

2.7. *Sodium thiosulfate stock solution 1.0N.* Dissolve 248.2 g. $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled distilled water and dilute to 1 liter. Preserve by adding 5 ml. chloroform or 1 g. NaOH per liter.

2.8. *Standard sodium thiosulfate solution, 0.025N.* Prepare by (*a*) diluting 25 ml. sodium thiosulfate stock solution to a liter, or (*b*) dissolving 6.025 g. $Na_2S_2O_3 \cdot 5H_2O$ in freshly boiled and cooled distilled water and diluting to 1 liter. Standard sodium thiosulfate solution may be preserved by adding 5 ml. chloroform or 0.4 g. NaOH per liter.

Standardization with bi-iodate. Dissolve approximately 2 g. potassium iodide, free from iodate, in an Erlenmeyer flask with 100 to 150 ml. distilled water, add 10 ml. 1 + 9 H_2SO_4, followed by exactly 20 ml. standard 0.025*N* bi-iodate solution. Dilute to 200 ml., and titrate the liberated iodine with the thiosulfate solution, adding starch toward the end of the titration when a pale straw color is reached. Exactly 20 ml. 0.025*N* thiosulfate should be required when the solutions under comparison are of equal strength. It is convenient to adjust the solution to exactly 0.025*N*. One ml 0.025*N* thiosulfate is equivalent to 0.2 mg. oxygen.

Standardization with dichromate. Same as above except that 20 ml. standard dichromate is used in place of the 0.025*N* bi-iodate. Place in the dark for 5 min., dilute to approximately 400 ml., and titrate with 0.025*N* thiosulfate, and in addition:

2.9. *Alkaline-iodine sodium azide reagent.* Dissolve 10 g. NaN_3 in 40 ml. distilled water. Add this solution with constant stirring to 950 ml. alkaline-iodide reagent.

2.10. *Potassium fluoride solution.* Dissolve 40 g. $KF \cdot 2H_2O$ in distilled water, and make up to 100 ml.

3. Procedure

3.1. To the sample as collected in a 250- to 300-ml. bottle add 2 ml.* $MnSO_4$ solution followed by 2 ml. alkaline-iodide reagent well below the surface of the liquid, stopper with care to completely exclude air bubbles, and mix by inverting the bottle several times. When the precipitate settles leaving a clear supernatant above the manganese hydroxide floc, repeat the shaking a second time. With sea water a 10-min. period of contact with the precipitate will be required. When settling has produced at least 100 ml. clear supernatant, carefully remove the stopper and immediately add 2.0 ml. conc. H_2SO_4 by allowing the acid to run down the neck of the bottle, restopper, and mix by gentle inversion until solution is complete. The iodine should be uniformly distributed throughout the bottle before decanting the amount needed for titration. This should correspond to 200 ml. of original sample

*Note: The change in volume of reagents is made because 2 ml. of reagents insure better contact of reagents and sample with less agitation. It is still permissible to use 1-ml. reagent quantities with 250-ml. bottles.

after correction for the loss of sample by displacement with the reagents has been made. Thus when a total of 4 ml. (2 ml. each of the manganous sulfate and alkaline-iodide reagents) is added to a 300-ml. bottle, the volume taken for titration should be

$$200 \times \frac{300}{300 - 4} = 203 \text{ ml.}$$

3.2. Titrate with 0.025*N* thiosulfate to a pale straw color. Add 1 to 2 ml. freshly prepared starch solution, and continue the titration to the first disappearance of the blue color. If the end point is overrun the sample may be back-titrated with 0.025*N* bi-iodate which is added dropwise or by an additional measured volume of sample. Correction for the amount of bi-iodate or sample should be made. Subsequent recolorations due to the catalytic effect of nitrites or to presence of traces of ferric salts which have not been complexed with fluoride should be disregarded.

4. Calculation

4.1. Since 1 ml. 0.025*N* $Na_2S_2O_3$ is equivalent to 0.2 mg. oxygen, the number of ml. of sodium thiosulfate used is equivalent to the mg/l of dissolved oxygen if a volume equal to 200 ml. of original sample is titrated.

4.2. If the results are desired in ml. of oxygen gas at 0°C. and 760 mm. pressure, the DO in mg/l is multiplied by 0.698.

4.3. To express the results as percent of saturation at 760 mm. atmospheric pressure, the solubility data in Table I may be used. Formulas for correcting the solubilities to barometric pressures other than mean sea level are given below the table. These corrections are satisfactory for elevations below 2,500 ft. and for temperatures below 25°C. At higher elevations and temperatures the barometric pressure must be corrected for the aqueous vapor pressure.

4.4. The solubility of dissolved oxygen in distilled water at any barometric pressure, P, temperature, t°C., and the saturated vapor pressure, u, for the given t°C., may be calculated between the temperatures of 0° and 30°C. by Equation I and between the temperatures 30° and 50°C. by Equation II as follows:

$$\text{I.} \quad \text{ml/l DO at } 0° \text{ to } 30°\text{C.} = \frac{(P-u) \times 0.678}{35 + t°\text{C.}}$$

$$\text{II.} \quad \text{ml/l DO at } 30° \text{ to } 50°\text{C.} = \frac{(P-u) \times 0.827}{49 + t°\text{C.}}$$

TABLE I

SOLUBILITY OF OXYGEN IN FRESH WATER AND IN SEA WATER OF STATED DEGREES OF SALINITY AT VARIOUS TEMPERATURES WHEN EXPOSED TO WATER-SATURATED AIR AT A TOTAL PRESSURE OF 760 mm. HG.

Dry air is assumed to contain 20.90% oxygen

Calculated by G. C. Whipple and M. C. Whipple from measurements of C. J. J. Fox

	Chlorides in Sea Water (parts per million)					Difference per 100 ppm Cl	Dissolved Oxygen in Chloride-free Water	
	0	5000	10000	15000	20000			
°C.	Dissolved oxygen in parts per million by wgt.					ppm	°C.	ppm
0	14.62	13.79	12.97	12.14	11.32	0.0165	30	7.6
1	14.23	13.41	12.61	11.82	11.03	.0160	31	7.5
2	13.84	13.05	12.28	11.52	10.76	.0154	32	7.4
3	13.48	12.72	11.98	11.24	10.50	.0149	33	7.3
4	13.13	12.41	11.69	10.97	10.25	.0144	34	7.2
5	12.80	12.09	11.39	10.70	10.01	.0140	35	7.1
6	12.48	11.79	11.12	10.45	9.78	.0135	36	7.0
7	12.17	11.51	10.85	10.21	9.57	.0130	37	6.9
8	11.87	11.24	10.61	9.98	9.36	.0125	38	6.8
9	11.59	10.97	10.36	9.76	9.17	.0121	39	6.7
10	11.33	10.73	10.13	9.55	8.98	.0118	40	6.6
11	11.08	10.49	9.92	9.35	8.80	.0114	41	6.5
12	10.83	10.28	9.72	9.17	8.62	.0110	42	6.4
13	10.60	10.05	9.52	8.98	8.46	.0107	43	6.3
14	10.37	9.85	9.32	8.80	8.30	.0104	44	6.2
15	10.15	9.65	9.14	8.63	8.14	.0100	45	6.1
16	9.95	9.46	8.96	8.47	7.99	.0098	46	6.0
17	9.74	9.26	8.78	8.30	7.84	.0095	47	5.9
18	9.54	9.07	8.62	8.15	7.70	.0092	48	5.8
19	9.35	8.89	8.45	8.00	7.56	.0089	49	5.7
20	9.17	8.73	8.30	7.86	7.42	.0088	50	5.6
21	8.99	8.57	8.14	7.71	7.28	.0086		
22	8.83	8.42	7.99	7.57	7.14	.0084		
23	8.68	8.27	7.85	7.43	7.00	.0083		
24	8.53	8.12	7.71	7.30	6.87	.0083		
25	8.38	7.96	7.56	7.15	6.74	.0082		
26	8.22	7.81	7.42	7.02	6.61	.0080		
27	8.07	7.67	7.28	6.88	6.49	.0079		
28	7.92	7.53	7.14	6.75	6.37	.0078		
29	7.77	7.39	7.00	6.62	6.25	.0076		
30	7.63	7.25	6.86	6.49	6.13	.0075		

*Under any other barometric pressure, P, the solubility may be obtained from the corresponding value in the table by the formula:

$$S' = S\frac{P}{760} = S\frac{P'}{29.92}$$

in which S' = Solubility at P or P',
S = Solubility at 760 mm. or 29.92 in.,
P = Barometric pressure in mm., and
P' = Barometric pressure in in.

The second decimal place in the above table is not accurately known. The average difference from the mean of five different investigators represents 0.07 ppm. Until further data are obtained, however, the second decimal place has been retained in the table.

The solubility data for temperatures from 30° to 50°C. in the last column of Table I were calculated by Equation II.

5. Precision and accuracy

The dissolved oxygen in distilled water can be determined with a precision expressed as a standard deviation of 0.043 ml. ($n = 3$; 6×10) of 0.025N sodium thiosulfate, and in sewage and secondary effluents of 0.058 ml. ($n = 2$; 26×10). In the presence of appreciable interferences, even with the proper Winkler modification, the standard deviation may be as high as 0.1 ml. Even greater errors may occur in waters having organic suspended solids or heavily polluted waters. For many industrial wastes the tentative polarographic method may be desirable. Errors due to carelessness in collecting samples, prolonging the completion of the test, and the improper selection of a modified Winkler test should be avoided.

Reference: *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes.* Tenth edition, 1955. APHA-AWWA-FSIWA. pp. 250-56.

OXYGEN, BIOCHEMICAL DEMAND (METHOD M3)

The biochemical oxygen demand, BOD, of sewage, sewage effluents, polluted waters, or industrial wastes is the quantity of dissolved oxygen, in mg/l, required during stabilization of the decomposable organic matter by aerobic biochemical action. Determination of this quantity is accomplished by diluting suitable portions of the sample with water saturated with oxygen and measuring the dissolved oxygen in the mixture both immediately and after a period of incubation, usually 5 days, under favorable conditions for such action. Complete stabilization requires more than 100 days at 20°C., but such long periods of incubation are impracticable in any but research investigations. Consequently, the 5-day period is recommended as the standard procedure. Conversion of the data from one incubation period to another, or from one temperature to another, may be approximated only after special studies have been made.

Interference

It is essential that uninhibited growth of both bacteria and plankton occur in the diluted samples. Reliable results cannot be obtained if the diluted sample contains caustic alkalinity, mineral acid, free chlorine, or any other bactericidal substance. In such cases the bactericidal substance must be neutralized and the dilution water seeded with settled sewage.

In order to obtain comparable results from 2 or more dilutions, the dilution water must be free from an appreciable oxygen demand of its own and also must possess no germicidal properties due to residual chlorine, chloramines which may distill over, caustic alkalinity, or copper from the still or its condenser. The fact that most natural waters possess an appreciable 5-day demand at 20°C. has led to the use of a synthetic dilution water. Distilled water alone, and chemically treated tap waters, should not be used. Tap waters containing chlorine or chloramines should be passed through activated carbon filters before distillation to remove these volatile compounds.

In many BOD dilutions of polluted water nitrification occurs in less than 5 days of incubation. Thus, in many cases the 5-day BOD may not measure the carbonaceous oxidation alone. Nitrification requires dissolved oxygen. Under natural conditions nitrification might deplete the dissolved oxygen below a satisfactory level for fish and other biological forms. On the other hand, nitrates are sources of oxygen which allay septic conditions. Since sewage effluents undergoing incipient nitrification may produce higher 5-day BOD values than effluents which have been treated to a lesser degree, attempts have been made to revise the BOD technique so that it would measure only the carbonaceous BOD. Recent studies showing that the reproduction period of nitrite-forming organisms exceeds 24 hr. indicate that heat pasteurization, acidification, or 2 mg/l methylene blue in standard dilution water which is buffered to pH 6.25 with KH_2PO_4 may be useful for depressing nitrification in BOD dilutions of biological treatment plant effluents. If the original concept of a carbonaceous BOD is to be retained, then effluents of second-stage sewage treatment plants, particularly if unchlorinated, should be treated to depress or prevent nitrification. Studies in recent years indicate that the exponential rate of carbonaceous oxidation (k) at 20°C. rarely has a uniform value of 0.1 but varies from less than one-half to more than twice this value. This fact throws doubt on the calculation of the ultimate carbonaceous demand (L) of a sample from 5-day BOD values unless the k value has been determined on the sewage, waste, or stream under consideration.

DILUTION METHOD FOR SEWAGE

1. Apparatus

1.1. *Incubation bottles, 250- to 300-ml. capacity with ground-glass stoppers.* They should be cleaned with chromic acid mixture, carefully rinsed, and thoroughly drained before use. As a precaution against drawing air into the dilution bottle during incubation, a water seal is recommended. Satisfactory water seals are obtained by inverting the bottles in a water bath or adding water to the flared mouth of special BOD bottles.

1.2. *Air incubator or a water bath.* One thermostatically controlled at 20°C. ± 1°C. should be used. Light should be excluded to prevent formation of DO by algae in the sample.

2. Reagents

2.1. *Distilled water.* Water used for solutions and for preparation of the dilution water must be of highest quality, contain less than 0.01 mg/l copper, and be free of chlorine, chloramines, caustic alkalinity, or acids.

2.2. *Phosphate buffer solution.* Dissolve 8.5 g. KH_2PO_4, 21.75 g. K_2HPO_4, 33.4 g. $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g. NH_4Cl in about 500 ml. distilled water, and dilute to 1 liter. The pH of this buffer should be 7.2 without further adjustment.

2.3. *Magnesium sulfate solution.* Dissolve 22.5 g. $MgSO_4 \cdot 7H_2O$ in distilled water, and dilute to 1 liter.

2.4. *Calcium chloride solution.* Dissolve 27.5 g.anhydrous $CaCl_2$ in distilled water and dilute to 1 liter.

2.5. *Ferric chloride solution.* Dissolve 0.25 g. $FeCl_3 \cdot 6H_2O$ in distilled water, and dilute to 1 liter.

2.6. *Acid and alkali solutions, approximately 1N.* For neutralization of waste samples which are either caustic or acidic.

2.7. *Sodium sulfite solution, approximately 0.025N.* Dissolve 1.575 g. anhydrous Na_2SO_3 in 1,000 ml. distilled water. This solution is not stable and should be prepared frequently.

2.8. *Seeding material.* A satisfactory seed may be obtained by using the supernatant liquor from domestic sewage which has been stored at 20°C. for 24 to 36 hr.

In the case of many industrial wastes, a more correct estimation of the actual BOD may be obtained if the receiving water taken some distance below the point of discharge or other acclimated seed is used for seeding material. Nitrification, however, may be encouraged when using natural waters for seeding purposes, and this possibility should be considered when interpreting the results.

Strictly fresh raw sewage does not represent the ideal in seed because the organisms present are characteristic of excrement and other concentrated wastes, and the organisms active in the oxidation of sewage have not had time to multiply. A partially stale, settled sewage should be used. This is obtained by the incubation of raw sewage at 20°C. in an open bottle for 24 to 36 hr.

Some industrial wastes may have toxic or inhibitory concentrations of suspected or unknown elements in the BOD dilutions incubated. Usually the inhibitory substances are neutralized, if possible, and the dilution water is seeded with general flora and fauna from sewage which has stood at room temperature 24 hr. Under natural purification, the same or higher concentra-

tion of the toxic substance may not be inhibitory because acclimated flora and fauna may have developed in the receiving stream. It is obvious, therefore, that the sewage seed selected may be entirely inadequate and that the use of river or lake water, polluted with the same waste under test, may provide a much more satisfactory seed.

3. Procedure

3.1. *Preparation of dilution water.* The distilled water used should be as near 20°C. as possible and of highest purity. Place the desired volume of distilled water into a suitable bottle, and add 1 ml. each of phosphate buffer, magnesium sulfate, calcium chloride, and ferric chloride solutions for each liter of water.

3.2. Seed the dilution water if necessary by adding 1 to 10 ml. settled domestic sewage, 24 to 36 hr. old, per liter. If it is desired to use river water for seeding purposes, 10 to 50 ml. river water per liter should be used. The amount of seeding material in either case should be chosen in the light of past experience so as to give oxygen depletions in the blanks of at least 0.6 mg/l in 5 days' incubation. Seeded dilution water should be used the day it is made. Aerate the dilution water with a clean supply of compressed air to saturate with oxygen. Saturation may also be obtained by 2 to 3 days' storage in partially filled bottles which are closed with a cotton plug.

3.3. *Pretreatment*

a. Samples containing caustic alkalinity or acid should be neutralized to about pH 7.0 with 1*N* H_2SO_4 or NaOH using a pH meter or bromthymol blue as an outside indicator. The pH of the seeded dilution water should not be changed by the preparation of the lowest dilution of sample.

b. Samples containing residual chlorine compounds also require pretreatment. If the samples are allowed to stand for 1 to 2 hr., the residual chlorine will often be dissipated. BOD dilutions can then be prepared with properly seeded standard dilution water. Higher chlorine residuals in neutralized samples should be destroyed by adding sodium sulfite. The appropriate quantity of Na_2SO_3 is determined on a 100- to 1,000-ml. portion of the sample by adding 10 ml. of 10% KI solution and titrating with 0.025N Na_2SO_3 to the starch-iodide end point. Add to a volume of sample the quantity of Na_2SO_3 determined by the above test, mix, and after 10 to 20 min. test aliquot samples for residual chlorine to check the treatment. Prepare BOD dilutions with seeded standard dilution water.

c. Samples containing other toxic substances, such as those from industrial wastes, frequently require special study and treatment, for example, plating out of toxic metals on electrodes.

d. Samples supersaturated with dissolved oxygen, over 9.17 mg/l at 20°C., may be encountered during winter months or in localities where algae are actively growing. To prevent loss of oxygen during incubation of these samples the DO should be reduced to saturation by bringing the sample to about 20°C. in a partly filled bottle and agitating it by vigorously shaking or by aerating with compressed air.

3.4. *Dilution technique.* Make several dilutions of the prepared sample to cover the range of depletions expected, usually 0.1 to 1.0% of strong trade wastes, 1 to 5% of normal and settled sewage, 5 to 25% of oxidized effluents, and 25 to 100% of polluted river waters. This dilution may be accomplished as follows: Carefully siphon standard dilution water, seeded if necessary, into a graduated cylinder of 500 to 1,000 ml. capacity, filling the cylinder half full without entrainment of air. Add the quantity of carefully mixed sample to make the desired dilution, and fill to the 500- or 1,000-ml. mark with dilution water. Mix well with a plunger-type mixing rod, avoiding the entrainment of air. Siphon the mixed dilution into 2 incubation bottles, 1 for incubation and the other for determination of the initial dissolved oxygen in the mixture, stopper tightly, and incubate for 5 days at 20°C. The BOD bottles should be water-sealed by inversion in a tray of water in the 20°C. incubator or by using a special water-seal bottle. Prepare succeeding dilutions of lower concentration in the above manner or by adding dilution water to the unused portion of the preceding dilution.

Direct dilution technique. The direct dilution technique is greatly simplified when suitable amounts of sample are measured directly into bottles of known capacity with a large tipped volumetric pipet and the bottle filled with just sufficient dilution water so that the stopper can be inserted without leaving air bubbles. Dilutions greater than 1 to 100 should be made by diluting the waste in a volumetric flask before it is added to the incubation bottles for final dilution.

3.5. *Determination of dissolved oxygen.* If the sample represents 1% or more of the lowest BOD dilution, determine DO on the undiluted sample. This determination is usually omitted on sewage and settled effluents known to have a dissolved oxygen of practically zero.

3.6. *Incubation.* The blank dilution water and the diluted samples are incubated for 5 days at 20°C., and then the DO is determined in the incubated samples and the blank, using the Alsterberg azide modification of the Winkler method. In special cases other modifications may be necessary. Those dilutions showing 40 to 90% depletion of the initial oxygen content shall be considered most reliable. Those dilutions showing a residual dissolved oxygen of less than 1 mg/l or a depletion of less than 2 mg/l will be unreliable.

3.7. *Seed correction.* If the dilution water is seeded, determine the oxygen depletion of the settled sewage used for seeding in a 1% to 5% dilution which should result in 40 to 70% oxygen depletion in 5 days. This depletion is then used to calculate the correction due to the smaller amount of seed in the dilution water, and not the DO in the seeded blank which has been incubated for 5 days. This method of correction is preferred because the 5-day seeded dilution water blank is subject to erratic oxidation which is not characteristic in the seeded sample and which is due to the very high dilution of the seed.

3.8. *Dilution water control.* Fill 2 BOD bottles with unseeded dilution water. Stopper and fill the seal of 1 for incubation. The other bottle is for determining the dissolved oxygen before incubation. The dissolved-oxygen results on these 2 bottles are used as a rough check of the quality of the unseeded dilution water. The depletion obtained should not be used as a blank correction and should not be more than 0.2 ml. and preferably not more than 0.1 ml.

3.9. *Method of checking quality of dilution water for presence of toxic substances and viability of seeding material.* The BOD test is a bio-assay procedure and, consequently, the results obtained are influenced greatly by the presence of toxic substances or the use of an impotent seeding material. Experience has taught that distilled waters are frequently contaminated with toxic substances, most often copper, and that some sewage seeds are relatively inactive. The results obtained with such waters are always low. If nitrifying organisms are present in the seeding matter, the results will usually be high.

The quality of the dilution water and/or seed can be established by using known solutions of pure organic substances as test substrates. Prepare a standard solution containing 300 mg/l of glucose or glutamic acid. Use these solutions separately or mixed in equal proportions. Pipet portions of 5.0 to 10.0 ml. of the solution into calibrated incubation bottles, fill with the seeded dilution water, and incubate with the seed control at 20°C. for 5 days.

The standard glucose solution should show a BOD of 224 ± 11 mg/l, the standard glutamic acid solution should show a BOD of 217 ± 10 mg/l, and the mixture should have a BOD of 220 ± 10 mg/l. Any appreciable divergence from these results should raise serious question concerning the quality of the distilled water or the viability of the seeding material. Further, a variation greater than ± 20 to 22 mg/l should not occur more frequently than 5% of the time or the technique used is subject to improvement.

On the basis of a mixed primary standard containing 150 mg/l each of glucose and glutamic acid, the 5-day BOD varies in magnitude according to the type of seed, and precision varies with the quality of seed, as shown in the tabulation below.

Excepting the oxidized river water and effluents, a low seed correction resulted in an appreciably higher value for σ. Each seed source should be checked to determine the amount required to obtain optimum precision. If results differ appreciably from those given in the tabulation after considering the seed source, the technique is questionable.

4. The immediate dissolved oxygen demand

Occasionally, as for example, in wastes or waters containing sulfide, sulfite, or ferrous ions, it is desirable to differentiate between the immediate dissolved oxygen demand, IDOD, and the true biochemical oxygen demand. The depletion of DO in a standard water dilution of the sample in 15 min. has been arbitrarily selected as the IDOD. To determine the IDOD the DO of the sample and the DO of the dilution water are determined separately. An appropriate dilution of sample and dilution water is prepared, and the DO is determined after 15 min. The calculated DO of the sample dilution minus the observed DO after 15 min. is the IDOD in mg/l of the sample dilution. If this value represents a substantial figure, it should be distinguished from the BOD and reported separately.

5. Calculations

Legend of symbols

D_0 = DO of original dilution water
D_1 = DO in diluted sample 15 min. after preparation
D_2 = DO of the diluted sample after incubation
S = DO of original undiluted sample
Dc = DO available in dilution at zero time $(D_0 \times p) + (S \times \overline{P})$
p = decimal fraction of dilution water used
$\overline{P}$ = decimal fraction of sample used
Seed Correction = When dilution water must be seeded
B_1 = DO of the dilution of seed control before incubation
B_2 = DO of the dilution of seed control after incubation
f = ratio of seed in the sample to seed in the control =

$$\frac{\text{percent seed in } D_1}{\text{percent seed in } B_1}$$

Seed correction $= (B_1 - B_2)f$

5.1. *Biochemical oxygen demand*

a. When seeding is not required

$$\text{mg/l BOD} = \frac{D_1 - D_2}{\overline{P}}$$

b. When using seeded dilution water

$$\text{mg/l BOD} = \frac{(D_1 - D_2) - (B_1 - B_2) \times f}{\overline{P}}$$

c. If the IDOD is small or not determined, it is included in total BOD

$$\text{mg/l BOD} = \frac{Dc - D_2}{\overline{P}}$$

5.2. *Immediate dissolved oxygen demand*

$$\text{mg/l IDOD} = \frac{Dc - D_1}{\overline{P}}$$

The dissolved oxygen determined on the unseeded dilution water after incubation is not used in the BOD calculations because this practice overcorrects for the dilution water. In all the above calculations corrections are not made for small losses of dissolved oxygen in the dilution water during incubation. If the dilution water is unsatisfactory, proper corrections are difficult and the results are questionable.

Type of Seed	5-Day Seed Correction mg/l	Mean 5-Day BOD mg/l	σ mg/l
Settled fresh sewage	>0.6	218	±11
Settled stale sewage	>0.6	207	±8
River waters, 4 different sources	0.05 to 0.22	224 to 242	±7 to 13
Activated sludge effluent	0.07 to 0.68	221	±13
Trickling filter effluent	0.2 to 0.4	225	±8

6. Precision and accuracy

There is no standard against which the accuracy of the BOD test can be measured. The precision of the dissolved oxygen determination on which the BOD test is based and of the incubated samples of diluted standards, sewages, and effluents is expressed as standard deviation in ml. of 0.025N thiosulfate as follows:

DO in dilution water

σ = 0.043 ml. (n = 3; 6 × 10)

DO in sewage

σ = 0.058 ml. (n = 2; 26 × 10)

Incubated BOD samples
1- to 20-day BOD's (curve)
Glucose and glutamic acid
$\sigma = 0.079$ ml. ($n = 1$; 9 (3×10)

5-day BOD
Raw sewage
$\sigma = 0.112$ ml. ($n = 3$; 38×10)
Settled sewage
$\sigma = 0.071$ ml. ($n = 1$; 20×5 conc.)
Activated sludge effluent
$\sigma = 0.084$ ml. ($n = 3$; 30×10)
Trickling filter effluent
$\sigma = 0.075$ ml. ($n = 1$; 16×5)

These data indicate that where interfering and toxic substances are absent the standard deviation of the BOD test on sewages and effluents may range from 0.07 to 0.11 ml. oxygen demand titrated. This should also hold true on wastes from food-processing industries or other organic nontoxic wastes.

Industrial wastes containing toxic materials and/or substances which interfere with the DO determination have not been studied statistically.

Reference: *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes.* Tenth edition, 1955. APHA-AWWA-FSIWA. pp. 260–66.

RESIDUE (METHOD M4)

The results on total, volatile, and fixed residues are subject to considerable error because of losses of volatile compounds during evaporation and of carbon dioxide and volatile minerals during ignition, and because of the presence of calcium oxide in the ash. Results for residues high in oil or grease content may be of questionable value due to the difficulty of drying to constant weight in a reasonable time.

In the interpretation of results these possible sources of error must be recognized.

A. Residue on Evaporation

1. General discussion

The determination of residue by evaporation may be of limited value for estimating the effect of an effluent on receiving water, but it may be useful

as a control in plant operation. A large number of solids crystallize as hydrates, which lose water at various temperatures and form decomposition products before all their water of hydration is given off. This is true also of various colloidal suspensions. In addition, volatile compounds are lost during evaporation and ignition. It is essential for the analyst to understand that the procedure given for residue on evaporation is quite arbitrary and the results generally will not represent the weight of actual dissolved and suspended solids.

2. Procedure for residue on evaporation

2.1. Evaporate 100 ml. sample in an ignited and tared dish, dry to a constant weight at 103°C., cool in desiccator, and weigh. Drying for 1 hr. at 103°C. is usually sufficient. On samples with a pH below 4.3, NaOH is added, and a pH of 4.3 is maintained during evaporation. The amount of Na added is subtracted from the weight of residue.

3. Calculation

$$\text{mg/l residue on evaporation} = \frac{\text{mg. residue} \times 1{,}000}{\text{ml. sample}}$$

4. Precision and accuracy

The accuracy of all the solids determinations in sewage and industrial waste is not determinable because there is no universal standard against which the accuracy can be determined. When the residue from a 50- to 100-ml. sample of raw sewage was weighed, the standard deviation of the weighing was found to be 1.9 mg. ($n = 3$; 60×10), but these data are considered statistically unreliable probably due to sampling errors. On settled effluents standard deviation of 0.9 mg. ($n = 1$; 5×20) was statistically reliable.

5. Procedure for total volatile and fixed residue

Total volatile and fixed solids are determined by igniting the above total solids at 600°C. in an electric muffle to constant weight, usually requiring 10 to 15 min. The mg. loss on ignition per liter shall be reported as mg/l volatile solids and the mg. residue per liter as mg/l fixed solids. Calculate as above.

6. Precision and accuracy

Using the above procedure, the standard deviation of the weighing was found to be 1.5 mg. ($n = 2$; 50×10), but these data are considered statistically unreliable, probably due to sampling errors.

B. Suspended Matter

1. General discussion

Suspended matter is best determined by filtration through an asbestos mat in a Gooch crucible. However, for a rapid determination of suspended matter, particularly of mixed liquor in activated sludge plants, the aluminum dish method, as follows, may be used.

ALUMINUM DISH METHOD

1. Apparatus

1.1. *Aluminum dish*, with a perforated bottom similar to a Buchner funnel, inside diameter 92 mm., height 25 mm.

1.2. *Filter paper*, 90 mm. diameter. E.D. No. 615, Whatman No. 1, or equal.

1.3. *Sponge rubber ring*, 93 mm. outside diameter, 75 mm. inside diameter, thickness about 3 mm.

1.4. *Buchner funnel*, No. 2A, inside diameter at bottom, 93 mm.

1.5. *Filter flask*, with side tube, 1,000-ml. size.

2. Procedure

Dry dish and filter paper in oven. Cool in desiccator and weigh. Wet the filter paper, place the dish with paper on rubber ring in Buchner funnel, and apply about 20 in. of vacuum to the flask. Immediately add 20 to 100 ml. of sludge which should yield 0.2 to 0.4 g. of dry solids to dish, and after the water has been extracted, dry in oven for about 30 min. at 103° to 105°C. Cool in desiccator and weigh.

The test is applicable to aeration tank-mixed liquor, in which case it is reported as percent suspended matter, or to heavier sludges, such as return sludges, when it is reported as percent of dry sludge solids.

3. Precision and accuracy

Standard deviation was 0.6 mg. on 100-ml. sample ($n = 1$; 21×10).

ASBESTOS MAT METHOD

1. Apparatus

1.1. *Gooch crucible, 30 ml.*

1.2 *Suction apparatus.*

2. Reagents

2.1. *Asbestos cream.* Prepare a cream with distilled water by adding 15 g. acid-washed, medium-fiber asbestos which is prepared particularly for Gooch

crucible determinations to 1,000 ml. distilled water. Some asbestos sold for this purpose contains too much fine asbestos powder. This fine material should be removed by repeated decantations.

3. Procedure

3.1. An asbestos fiber mat is prepared in a 30-ml. Gooch crucible by adding sufficient homogeneous suspension of the asbestos cream, approximately 0.3 g. dry-weight asbestos, to produce a mat 3 mm. thick with gentle suction. Wash with 100 ml. distilled water, dry at 103°C. for 1 hr., cool in desiccator, and weigh. If volatile matter is to be determined by ignition, the crucible and mat must be ignited, cooled, and weighed.

(Note: The amount of suspended matter removed during filtration depends on the thickness of the asbestos mat used in the Gooch crucible. Accordingly, a mat thickness of 3 mm. is arbitrarily established in this procedure, and the importance of uniform mat thickness should be recognized.)

3.2. Measure out 50 to 100 ml. well-mixed sample with a wide-tip pipet or measuring flask, and filter through the weighed Gooch crucible using suction. Wash with distilled water, dry at 103°C. for 1 hr., cool in a desiccator, and weigh.

4. Precision and accuracy

The precision expressed as standard deviation was found to be as follows:

Sewage and some industrial wastes = 1.4 mg. ($n = 3$; 65×10)

Settled sewage = 0.4 mg. ($n = 3$; 39×10)

5. Procedure for volatile and fixed suspended matter

The volatilization of organic matter, carbonates, and ammonium salts from sewage solids is subject to a great many errors. It should be done in an electric muffle furnace at 600°C.

5.1. Ignite the suspended matter for 10 to 15 min. Cool in desiccator and reweigh. Report the mg. lost on ignition per liter as mg/l volatile suspended matter and the mg. ash per liter remaining as mg/l fixed suspended matter.

6. Precision and accuracy

On most of the volatile and fixed suspended matter determined as above, the standard deviation was found to be 0.6 mg. ($n = 3$; 49×10).

C. Dissolved Matter

Dissolved matter may be obtained by difference between the total residue and suspended matter, or it may be determined by evaporating a filtered sample as directed for residue on evaporation, Sec. A.2.

D. Settleable Matter

1. General discussion

Settleable matter may be determined and reported on a volume or weight basis.

2. Procedure

2.1. *By volume.* Fill an Imhoff cone to the liter mark with a thoroughly mixed sample. Settle for 45 min., gently stir the sides of the cone with a rod or by spinning, settle 15 min. longer, and record the ml. of settleable matter in the cone.

2.2. *By weight.* This technique defines settleable matter as that matter in sewage which will not stay in suspension during the settling period either by virtue of settling to the bottom or floating to the top.

Determine the suspended matter in a sample of the sewage under investigation, as directed in B.

Pour a well-mixed sample of the sewage into a glass vessel not less than 9 cm. in diameter, using a quantity of sample not less than 1 liter and sufficient to insure a depth of 20 cm. A glass vessel of greater diameter and larger volume of sample may be used. Allow to stand quiescent for 1 hr., and without disturbing the settled material or that which may be floating, siphon 250 ml. sample from the center of the container at a point halfway between the surface of the settled sludge and the liquid surface. Determine the suspended matter in mg/l in all or in an aliquot portion of this supernatant liquor as directed in B. This value in mg/l is equivalent to the nonsettling matter.

3. Calculation

mg/l by weight of settleable matter = mg/l suspended matter − mg/l nonsettling matter

Reference: *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes.* Tenth edition, 1955. APHA-AWWA-FSIWA. pp. 270–72; 354.

pH VALUE (METHOD M5)
(GLASS ELECTRODE METHOD)

1. General discussion

1.1. *Principle.* Several types of electrodes have been suggested for the electrometric determination of pH. Although the hydrogen gas electrode is recognized as the primary standard, the glass electrode in combination with the reference potential provided by a saturated calomel electrode is most generally used. The glass electrode system is based on the fact that a change of 1 pH unit produces an electrical change of 59.1 millivolts at 25°C.

1.2. *Interference.* The glass electrode is relatively immune to interference from color, turbidity, colloidal matter, free chlorine, oxidants, or reductants, as well as high saline content, except for a sodium error at high pH. The error caused by high sodium ion concentrations at a pH above 10 may be reduced by using special "low sodium error" electrodes. When employing ordinary glass electrodes, approximate corrections for the sodium error may be made by consulting a chart which the manufacturer can furnish for the particular make and catalogue number of electrode. Temperature exerts two significant effects on pH measurements: (1) the electrodes themselves vary in potential with temperature, and (2) ionization in the sample varies with temperature. The first effect can be compensated by an adjustment which is provided on the better commercial instruments. The second effect is inherent in the sample and is taken into consideration by recording both the temperature and the pH of each sample.

2. Apparatus

Where flow-type electrodes are unavailable, or where stirring may be inadequate as in the case of ordinary immersion (dipping)-type electrodes, the best procedure is to wash the glass electrode 6 or 8 times with portions of the sample, particularly when an unbuffered measurement follows one on a buffered solution. Flow-type electrodes are recommended for the accurate measurement of relatively unbuffered waters such as condensates. Measurements on buffered waters can be obtained on open samples. Equilibrium should be established between the sample and the electrode system as shown by the absence of drift, before readings are accepted as final. If the water is hot or if the pH is over 10, special glass electrodes should be used, and the assembly should be standardized under conditions of temperature and concentration as close as possible to those of the sample, taking into account the manufacturer's recommendations. The analyst should constantly be on the alert for possible erratic results arising from mechanical or electrical failures such as weak batteries, cracked glass electrodes, plugged liquid junction, and fouling of the electrodes with oily or precipitated materials.

3. Buffer solutions

Electrode systems are calibrated against buffer solutions of known pH value. Since buffer solutions may deteriorate because of mold growth or through contamination, it may be advisable to prepare them freshly as needed by dissolving dry buffer salts in distilled water. Commercially available buffer tablets or powders of tested quality may also be used. It is good practice to calibrate the electrodes with a buffer whose pH is close to that of the samples, so as to minimize any error resulting from nonlinear response of the electrode. In making up buffers from solid salts, it is imperative that all of the material be dissolved, otherwise the pH may be incorrect. Polyethylene bottles are preferable for the storage of buffers and samples, although pyrex glassware may be employed. Limitations of space permit information on the preparation of only 3 buffer solutions at practically spaced intervals, pH 4, 7, and 9, for standardization purposes and for checking the linearity of electrode response.

In general, analytical reagent-grade chemicals are satisfactory for the preparation of the following buffer solutions. Where a high degree of accuracy is required, however, it is advisable to use salts of buffer quality supplied by the National Bureau of Standards. The pH values of 3 buffer solutions at the indicated temperatures are listed in Table II. The tabulated pH values were obtained with salts of the highest purity.

TABLE II

EFFECT OF TEMPERATURE ON pH VALUES OF BUFFER SOLUTIONS

Temperature °C.	pH 4 Buffer	pH 7 Buffer	pH 9 Buffer
0	4.01	7.08	9.46
5	4.01	7.05	9.38
10	4.00	7.02	9.33
15	4.00	7.00	9.27
20	4.00	6.98	9.22
25	4.01	6.96	9.18
30	4.01	6.95	9.14
35	4.02	6.94	9.10
40	4.03	6.94	9.07
45	4.04	6.93	9.04
50	4.06	6.93	9.01
55	4.08	6.94	8.98
60	4.10	6.94	8.96

3.1. *pH 4 buffer solution.* Dissolve 10.2 g. anhydrous potassium biphthalate, $KHC_8H_4O_4$, using boiled and cooled distilled water. Dilute to 1.0 liter.

3.2. *pH 7 buffer solution.* Dissolve 1.361 g. anhydrous potassium dihydrogen phosphate, KH_2PO_4, and 1.420 g. anhydrous disodium hydrogen phosphate, Na_2HPO_4, both of which have been dried overnight at 110° to 130°C. Use distilled water which has been boiled and cooled. Dilute to 1.0 liter.

3.3. *pH 9 buffer solution.* Dissolve 3.81 g. sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$, also called borax, using boiled and cooled distilled water. Dilute to 1.0 liter.

4. Procedure

Because of the differences between the many makes and models of pH meters which are available commercially, it is impossible to provide detailed instructions for the correct operation of every instrument. In each case the manufacturer's instructions must be followed. The glass electrode and the calomel electrode should be thoroughly wetted and prepared for use in accordance with the given instructions. The instrument can be standardized against a buffer solution with a pH approaching that of the sample, and then the linearity of electrode response can be checked against at least 1 additional buffer of a different pH. The readings with the additional buffers will afford a rough idea of the limits of accuracy to be expected of the instrument and the technique of operation.

5. Precision and accuracy

The precision and accuracy attainable with a given pH meter will depend upon the type and condition of the instrument employed and the technique of standardization and operation. With the proper care a precision of 0.02 pH unit and an accuracy of 0.05 pH unit can be achieved with the better battery models. Line-operated instruments, on the other hand, are less accurate, 0.1 pH unit representing the limits of accuracy under normal conditions.

Also see ALCA Official Methods B20 and F60 with proper exceptions to application to effluents.

Reference: *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes* pp. 161–63. Tenth edition, 1955. APHA–AWWA–FSIWA, pp. 161–63.

NITROGEN, ORGANIC (METHOD M6)

The Kjeldahl method, using copper sulfate and selenium granules as a catalyst, and potassium or sodium sulfate to raise the boiling point of the sulfuric acid, is recommended as the standard procedure. In most sewages, however, the addition of selenium granules or potassium or sodium sulfate may be eliminated from the digestion procedure. Direct Nesslerization is unsatisfactory. Distillation into standard acid or boric acid is necessary where accuracy is desired.

1. Reagents

1.1. *Phosphate buffer solution, 0.5M.* Dissolve 14.3 g. anhydrous KH_2PO_4 and 68.8 g. anhydrous K_2HPO_4 in ammonia-free water, and dilute to 1 liter.

1.2. *Sulfuric acid, concentrated.* Low in nitrogen.

1.3. *Copper sulfate solution.* Dissolve 100 g. $CuSO_4 \cdot 5H_2O$ in ammonia-free water, and dilute to 1 liter.

1.4. *Sodium hydroxide solution.* Dissolve 500 g. NaOH in ammonia-free water, and dilute to 1 liter.

1.5. *Boric acid solution.* Dissolve 40 g. H_3BO_3 in 1 liter of ammonia-free water.

1.6. *Standard sulfuric acid solution, 0.02N.* 1 ml. = 0.28 mg. N. Other strengths of standard acid may be used.

1.7. *Methyl red indicator.* Dissolve 0.1 g. methyl red in 7.4 ml. 0.05*N* NaOH, and dilute to 100 ml. with distilled water.

1.8. *Sodium or potassium sulfate, anhydrous.*

1.9. *Selenium, Henger granules.*

2. Procedure

2.1. Measure 100 ml. or more of sample into an 800-ml. Kjeldahl flask, dilute to 300 ml., neutralize to pH 7 if necessary, and add 25 ml. phosphate buffer solution. Boil or distill off the free ammonia. The residue from the free ammonia determination may be used.

2.2. Add 10 ml. conc. H_2SO_4 and 1 ml. $CuSO_4$ solution. The addition of 2 or 3 Henger selenized granules will aid in the destruction of organic matter and also prevent bumping. They are not necessary with sewage but may be with strong wastes. If the organic matter is hard to destroy, add 20 ml. conc. H_2SO_4, 5 g. K_2SO_4 or Na_2SO_4, and selenium granules. Digest by boiling in a

hood for 20 to 30 min. after the solution has become clear. Cool and add about 250 ml. ammonia-free water.

2.3. Make alkaline with sodium hydroxide using phenolphthalein as an indicator, and distill into 50 ml. H_3BO_3 solution, until about 200 ml. distillate has been obtained. Add 3 drops methyl red indicator, and titrate the ammonia with 0.02*N* H_2SO_4, matching the end point with that of a blank containing the same amounts of boric acid and indicator diluted to the same volume with carbon dioxide–free distilled water.

2.4. A blank should be run on the reagents used and necessary corrections made. Distillation into standard 0.02*N* acid and back-titration with standard 0.02*N* base may be used if preferred, but the boric acid procedure is simpler.

3. Calculation

$$\text{mg/l organic N} = \frac{\text{ml. } 0.02N \text{ acid} \times 0.28 \times 1{,}000}{\text{ml. sample}}$$

4. Precision and accuracy

Accuracy of recovery: 99 to 100%. Precision: the standard deviation was found to be 0.16 ml. of 0.02*N* acid, equivalent to 0.45 mg/l if 100 ml. sample of sewage containing from 10 to 50 mg/l organic nitrogen was used ($n=2$; 15×5).

Reference: *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes.* Tenth edition, 1955. APHA-AWWA-FSIWA. pp. 247–48.

SULFIDE (METHOD M7)

In sewage analysis determinations of 3 forms of sulfides are significant.

Total sulfides include the dissolved H_2S, HS^-, and S^{--}, as well as acid-soluble metallic sulfides present as suspended matter. The only common acid-insoluble metallic sulfide is that of copper.

Dissolved sulfides are those remaining after the suspended solids have been removed by flocculation and settling.

Un-ionized hydrogen sulfide is calculated from the concentration of dissolved sulfides and the pH of the sample.

The titrimetric method and the colorimetric method may be used to determine all 3 forms and are applicable to water, sewage, and industrial wastes.

Selection of method

The titrimetric method is the most accurate, but it cannot be carried out directly in sewage because of interfering substances. It is necessary to evolve the sulfides in a stream of gas and collect them in zinc acetate solution before titration. It can be applied only to solutions with sulfide concentrations above 1 mg/l. The colorimetric method is useful for the rapid determination of sulfides; it is especially recommended for low sulfide concentrations. The method is, however, designed for speed, sensitivity, and convenience rather than maximum accuracy. It is applicable to sulfide concentrations of 0.02 to 20 mg/l.

Titrimetric method

1. Reagents

1.1. *Zinc acetate solution.* Dissolve 240 g. Zn $(C_2H_3O_2)_2 \cdot 2H_2O$ in 1 liter distilled water.

1.2. *Sulfuric acid, concentrated.*

1.3. *Hydrochloric acid, concentrated.*

1.4. *Carbon dioxide.* Either a cylinder of CO_2 or a CO_2 generator.

1.5. *Starch solution.* Prepare as follows: An emulsion of 5 to 6 g. potato, arrowroot, or soluble starch is made in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few min., and let settle overnight. Use the clear supernatant. This solution may be preserved with 1.25 g. salicylic acid per liter or by the addition of a few drops of toluene.

1.6. *Sodium thiosulfate stock solution, 1.0N.* Dissolve 248.2 g. $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled distilled water, and dilute to 1 liter. Preserve by adding 5 ml. chloroform or 1 g. NaOH per liter.

1.7. *Standard sodium thiosulfate solution, 0.025N.* Prepare by (*a*) diluting 25 ml. sodium thiosulfate stock solution to a liter or (*b*) dissolving 6.205 g. $Na_2S_2O_3 \cdot 5H_2O$ in freshly boiled and cooled distilled water and diluting to 1 liter. Standard sodium thiosulfate solution may be preserved by adding 5 ml. chloroform or 0.4 g. NaOH per liter.

1.8. *Iodine solution, 0.025N.* Dissolve 20 to 25 g. KI in a little water, and add 3.175 g. iodine. After the iodine has dissolved, dilute to 1 liter, and standardize against 0.025*N* sodium thiosulfate using starch solution as indicator.

1.9. *Aluminum sulfate solution.* Dissolve 24 g. $Al_2(SO_4)_3 \cdot 18H_2O$ in distilled water, and dilute to 100 ml.

1.10. *Sodium hydroxide solution.* Dissolve 9 g. of NaOH pellets in distilled water, and dilute to 100 ml.

2. Collection of samples

Samples must be taken with a minimum of aeration, for not only are sulfides volatilized by aeration but any oxygen which is taken up destroys them by chemical action. Samples to be used only for total sulfide determination may be preserved by adding zinc acetate solution at the rate of 2 ml. per liter. This precipitates the sulfides as inert ZnS and also prevents further sulfide generation. Determinations of dissolved sulfides, and analyses of samples not preserved with zinc acetate, must be commenced within 3 min. of the time of sampling.

Samples to be used for determinations of total sulfides must contain a representative proportion of suspended solids.

3. Procedure for total sulfide

3.1. Introduce a measured volume of sample, usually approximately 500 ml., into a 1-liter aeration cylinder equipped with an alundum filter disc in the bottom, or a 1-liter wide-mouth bottle with a 2-hole stopper carrying a fritted-glass diffuser tube and an outlet tube. It is good practice to pass CO_2 gas through the apparatus, to displace oxygen, before introducing sample and acidifying. To the outlet, connect a 10-bulb absorption tube containing zinc acetate solution, or 2 125-ml. conical flasks, each containing about 5 ml. acetate solution diluted to 100 ml. and with suitable connections to pass the gas through them in series.

3.2. Acidify the sample with 10 ml. conc. H_2SO_4. Pass CO_2 or other inert gas (do not use air or O_2) through the sample for 1 hr., or until suitable tests show that no more sulfide is coming over.

3.3. To the zinc acetate solution add iodine solution well in excess of the amount necessary to react with the collected sulfides. One ml. 0.025*N* iodine is equivalent to 0.4 mg. sulfide.

3.4. Add 5 ml. conc. HCl, stopper, and shake. If 2 flasks are used, add nearly all the iodine to the first flask but half of the acid to each flask.

3.5. Transfer the liquid to a beaker and back-titrate with 0.025*N* $Na_2S_2O_3$, using starch solution as indicator. For accurate results a blank should be run on the reagents, especially if the sulfide content is low.

4. Calculation

$$\text{mg/l total sulfide as S} = \frac{(\text{ml } 0.025N \text{ iodine} - \text{ml. } 0.025N \text{ } Na_2S_2O_3) \times 400}{\text{ml. sample}}$$

5. Procedure for dissolved sulfide

Dissolved sulfides are determined on a sample from which the suspended solids have been removed by flocculating and settling.

5.1. Fill a 1-liter bottle with sample, flowing the liquid through the bottle after the manner of sampling for dissolved oxygen, in order to secure a sample which has had the least possible contact with air. Add 5 ml. $Al_2(SO_4)_3$ solution and 5 ml. NaOH solution, and stopper with no air bubbles under the stopper. Rotate back and forth about a transverse axis as vigorously as possible for at least a min. in order to flocculate the contents thoroughly.

5.2. Allow to settle for 15 min., or until the supernatant liquid is reasonably clear. Siphon a suitable portion of this liquid into the evolution apparatus as described under Sec. 3.1. Acidify, and proceed as for total sulfides.

6. Procedure for un-ionized hydrogen sulfide

6.1. Determine the pH of the original sample. Determine dissolved sulfides by the foregoing procedure. The concentration of un-ionized H_2S is found by multiplying the concentration of dissolved sulfides by a suitable factor as follows:

HYDROGEN SULFIDE FACTORS

pH	Factor	pH	Factor	pH	Factor
5.0	0.98	6.8	0.44	7.7	0.091
5.4	0.95	6.9	0.39	7.8	0.073
5.8	0.89	7.0	0.33	7.9	0.059
6.0	0.83	7.1	0.29	8.0	0.048
6.2	0.76	7.2	0.24	8.2	0.031
6.4	0.67	7.3	0.23	8.4	0.020
6.5	0.61	7.4	0.17	8.8	0.0079
6.6	0.56	7.5	0.14	9.2	0.0032
6.7	0.50	7.6	0.11	9.6	0.0013

These factors are applicable at a temperature of 25°C. For temperatures below 20°C. or above 30°C., or for sewages having a mineral solids content exceeding 2,000 mg/l, suitable corrections should be made.

Reference: *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes.* Tenth edition, 1955. APHA-AWWA-FSIWA. pp. 252–53; 273–74.

CHLORIDE (METHOD M8)

Chloride, in the form of Cl^- ion, is one of the major anions in water and sewage. The U. S. Public Health Service Drinking Water Standards of 1946 suggest that chloride shall not exceed an upper limit of 250 mg/l in acceptable water supplies.

Three methods are presented for the determination of chloride in potable water. The first two methods described, Volhard (A) and Mohr (B), are suitable for use when 0.15 to 10 mg. Cl is present in the portion of sample titrated. The tentative, mercurimetric method (C) is slightly more sensitive. Since the 3 methods are similar in most respects, selection is mostly a matter of preference.

A. Volhard Method

1. General discussion

1.1. *Principle.* Silver nitrate is added in excess to the acidified solution to precipitate the chloride. Without removing the precipitated silver chloride, the excess silver is titrated with thiocyanate in the presence of ferric ion and nitrobenzene. At the end point, red ferric thiocyanate is formed.

1.2. *Interference.* Iodide and bromide register as equivalent chloride concentration. Phosphate and sulfite do not interfere, but sulfide does.

2. Apparatus

2.1. *Erlenmeyer flasks, 250-ml., glass-stoppered.*

3. Reagents

3.1. *Standard sodium chloride solution, 0.0141N.* Dissolve 8.243 g. NaCl dried by fusing at 900°C. for one-half hr., in 500 ml. distilled water. Dilute 50.0 ml. to 1,000 ml. Each ml. of this solution contains 0.500 mg. Cl.

3.2. *Standard silver nitrate solution, 0.0141N.* Dissolve 2.396 g. $AgNO_3$ in 1 liter distilled water. Each ml. is equivalent to 0.500 mg. Cl. Using the procedure described below, standardize against the standard NaCl solution. The calculation is:

$$\text{Normality of } AgNO_3 = \frac{\text{mg. Cl}/35.46}{\text{ml. } AgNO_3 - (\text{ml. KCNS} \times F)}$$

where

$$F = \frac{\text{ml. } AgNO_3}{\text{ml. KCNS}} \text{ in absence of chloride}$$

3.3. *Potassium thiocyanate solution.* Dissolve 2 g. KCNS in 1 liter distilled water. Titrate against $AgNO_3$ standard solution using the method described in the procedure; distilled water should be used to bring the volume to 100 ml., and 10.0 ml. $AgNO_3$ solution should be added. Determine the ratio, F, of ml. $AgNO_3$ to ml. KCNS by the formula given above.

3.4. *Nitric acid, 1 + 1.* Boil and store in glass-stoppered brown bottle.

3.5. *Ferric alum solution.* Dissolve 25 g. $Fe_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ in 100 ml. distilled water.

3.6. *Nitrobenzene, purified.*

4. Procedure

To 100 ml. sample, or an aliquot diluted to 100 ml., add 5 ml. 1 + 1 HNO_3. Add $AgNO_3$ solution from a buret with mixing until an excess of approximately 2 ml. is present. Add 3 ml. nitrobenzene and 1 ml. ferric alum solution. Shake vigorously to coagulate the precipitate. Titrate the excess silver nitrate by adding standardized potassium thiocyanate, with shaking after each addition, until a permanent reddish color appears and does not fade after 1 min. of shaking.

5. Calculation

$$\text{mg/l Cl} = \frac{(\text{ml. } AgNO_3 - \text{ml. KCNS} \times F) \times \text{N of } AgNO_3 \times 35.46 \times 1{,}000}{\text{ml. sample}}$$

where

$$F = \frac{\text{ml. } AgNO_3}{\text{ml. KCNS}} \text{ in absence of chloride}$$

6. Precision and accuracy

The precision and accuracy are limited by the accuracy of detection of the end point, which is usually about 0.2 ml., or 0.1 mg. Cl, and by the presence of interfering substances.

Reference: *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes.* Tenth edition, 1955. APHA-AWWA-FSIWA. pp. 58–59.

Note: These methods are provisional ALCA methods as of June 17, 1959.

LIFE LINES

Brief Biographies of Our Contributors

BERNARD H. FOUQUET obtained his B.S. degree from American University, Washington, D. C., in 1955. The following year he joined the Leather Section of the National Bureau of Standards where he worked on the impregnation of leather with polymers and on other related problems. He joined ALCA in 1957. He is now employed in the Photographic Technological Section of NBS.

VICTOR MATTEI received his B.S. and M.S. degrees in chemistry in 1950 and 1952 respectively from Xavier University in Cincinnati, Ohio. He was associated with the Tanners' Council Research Laboratory from 1952 to 1958 conducting research on the fatliquoring of leather and the sulfation of fish oils. In July of 1958 he accepted a position in the central research laboratory of the A. C. Lawrence Leather Company and was associated with this company for 13 months. He is now employed in the Leather Chemical Division of Rohm & Haas Company doing research and development work on leather finishes.

WILLIAM T. RODDY, a graduate of the University of Cincinnati, has been associated with the Tanners' Council Research Laboratory for over 25 years. Since joining ALCA in 1939 he has been an active member, serving on the Physical Testing Committee, the Preparatory and Posttanning Processes Committee, and the Council. His numerous contributions to *JALCA* as well as other journals have added much to our knowledge of the structure of skin, beamhouse processes, tanning, and posttanning operations. Professor Roddy received the coveted Alsop Award at the 1957 ALCA Annual Meeting.

In a dry climate tanning can be avoided, as raw hide and skin putrefy very slowly under such circumstances. A few ancient Egyptian raw-hide articles have been found intact such as a twelfth-dynasty rectangular container moulded into shape and a four-string harp of about 1250 B.C., the body of which is covered with raw-hide.
—*Studies in Ancient Technology*, Vol. V. R. J. Forbes. Leiden: E. J. Brill, 1957.

Flint awls and knives, and bone implements and needles were the earliest leather-working tools. Certain fine-eyed Magdalenian needles must have been used to sew leather with fine leather thongs or strands of sinews. Sinew-dressing has been classed as a textile art and the Laplanders still produce twisted threads from sinews as delicate as fine yarn. Neolithic finds confirm this hypothesis. Primitive weaving was possibly carried out with thongs of leather as well as with vegetable fibres.
—*Studies in Ancient Technology*, Vol. V. R. J. Forbes. Leiden: E. J. Brill, 1957.

ALCA NEWS

Proceedings, Reports, Notices, and News

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ABSTRACTS

Australian Research on Wool. I. Structure and Chemistry of Wool. F. G. Lennox. *Research*, **12**, 82–90 (1958); abst. in *J. Soc. Dyers Colourists*, **75**, 267 (1959).—A review of the work done at the Melbourne laboratories of the Division of Protein Chemistry, C.S.I.R.O. C.L.D.

Reaction between Collagen and Polyfunctional Epoxides. R. L. Sykes. *Chem. and Industry*, **1959**, No. 23, 700–1.—Purified skin collagen and chemically modified collagens (O- and N-acetylated, deaminated, and esterified) were allowed to react with each of 5 epoxides at room temperature in buffer solutions (pH 3 to 12). The extent of cross-linking was measured by the increase in shrinkage temperature of the product. Only di- and tri-epoxides had any cross-linkage action on collagen; the effect was greater in alkaline solution. O- and N-aceylation had a large effect (but deamination and esterification only a minor one) in reducing the amount of cross-linkage. This fact suggests that the OH residues of hydroxyproline, serine, and threonine are involved in the reaction. C.L.D.

Investigations on the Bark Tannin of *Eucalyptus rostrata* of Israel. E. Karkauer, O. Elsner, and M. Lewin. *Leder Kurier*, **3**, 23–31 (1959).—Analyses of *Eucalyptus rostrata* bark by the American and by the French methods did not agree although they did agree for quebracho and other commercial materials. Analytical solutions containing 4 g. of tannin per l. could not be detanned completely; it was necessary to use solutions containing 2 g. per l. and to shake for 15 min. instead of 10. Results with French prechromed hide powder were identical with those with American hide powder only if the French powder was soaked overnight in 15 volumes of water, then squeezed to 71–74% moisture just before use. *E. rostrata* was introduced into Palestine from Australia about 70 years ago. Trees of average age (7–10 years) contained 12–16% tannin, and 5–6 year old trees about 9%. The entire bark, including the cork layer, was analyzed. Investigations in a temperature-controlled 2-l. flask showed that increasing the temperature up to boiling (97°C.) increased the amount of extracted solids and tannin. More material was extracted with soda, borax, or sulfite solutions than with water because of the higher pH. As concentration of the solvent increased up to 0.05*N* the amount of extracted material increased with borax and sulfite but was a maximum at 0.03*N* with soda. With sulfite there was a sharp increase in amount between 0.03 and 0.04*N*. Best results, in general, were found by extracting for 2 hr. at 80°C. with 0.05*N* sodium sulfite solution. Measurements of swelling and crushing strength indicate that clogging of extractors is possible. Swelling increased the volume of cubes over 75%. Cubes crushed at 160 kg/m² if dry, but if wet, not at 250 kg., the machine limit. The tannin was a mixture of tannins of the pyrogallol and catechol classes. Preliminary tanning tests on hide produced leather with a shrinkage temperature of 85°C. I.D.C.

Diamond Skin Disease, a Damage of Hog Skins. F. Stather and S. Walther. *Das Leder*, **10**, 73–4 (1959).—Swine erysipelas, a bacterial disease, may take either of 2 forms. In septicemia, which usually is fatal, the blood

stream is filled with bacteria and toxins, and the whole skin is red. Skins from such diseased animals do not appear on the market. A milder form of the disease is characterized by fever, loss of appetite, and, on the skin, sharply defined, square rhombic, reddish spots with 10–30 mm. sides. Leucocytes form the sharp boundary wall around the spots. In many animals the epidermis dies over the necrotic layer, then the stratum germinativum of healthy skin pushes under the dead parts and lifts the necrotic tissue. On flayed, unscalded, salted skins the damage is seen as dark, reddish-brown, tetragonal or rhombic spots which are harder than surrounding healthy tissue. Skins from scalded animals, after hair is removed, have intensely red spots similar to those on skin of the living animal; these spots are not hard. After tanning, the grain layer of the spots is found to be entirely gone. The surface is rough because it is composed of the coarse fibers of the lower corium layers. Such leather cannot be used for most purposes. I.D.C.

Problems of Vegetable Tanning. H. Herfeld. *Gerbereiwissenschaft und Praxis*, **1958**, May 15, 3–12.—A review of old and new methods of vegetable tanning and discussion of such factors as temperature, acidity and salt content of tan liquors, and use of dispersing agents. I.D.C.

Influence of Variations in Tanning Conditions on Water Affinity of Leather. H. Herfeld. *Leder und Häutenmarkt*, **1958**, 224 and 240.—Takeup of water by leather consists of surface wetting, filling of pores, and hydrophilic absorption by fibers. Absorption can be decreased by use of a short, strong lime so the skin is not opened too much, by a relatively heavy tannage (especially with vegetable tannin) and swelling with acid, by drying the leather at a relatively high temperature, oiling with solid fats, and use of certain finishing materials. Absorption and permeability are increased by wetting and emulsifying agents, staking, etc. I.D.C.

Ten Years of Sole Leather Tanning. H. Herfeld. *Gerbereiwissenschaft und Praxis*, **1959**, 3–16.—An address at the Vienna meeting of the Austrian Leather Technologists Assn. I.D.C.

Surface-active Agents in Chrome Leather Production. J. Strudwick. *J. Soc. Leather Trades' Chemists*, **43**, 146–59 (1959).—An explanation of surface activity is followed by a detailed description and classification of surface-active agents. Application of surface-active agents in soaking, liming, bating, and paraffin-degreasing of pickled stock is described. Paraffin-degreasing, aqueous-degreasing, and a method using reduced quantities of paraffin plus oleic acid with a nonionic agent were compared in a series of practical trials on haired sheepskins. The latter method gave an improved distribution of natural grease. Problems of mordanting glove leather and the uses of cationic and amphoteric agents to prevent loss of affinity for dyestuffs are discussed. Practical details are given of the use of surface agents in production of suede clothing and suede shoe leathers. J.M.C.

The Efficient Drying of Heavy Leather. N. Shaw and W. Davies. *J. Soc. Leather Trades' Chemists*, **43**, 160–75 (1959).—The engineering aspects of leather-drying are discussed primarily from a practical point of view. The

efficiency of drying methods is compared in terms of the quantity of steam in lb. required to remove 1 lb. of moisture from leather. An indication of the monetary savings to be expected when controlled drying methods replace uncontrolled methods is given. Various types of drying are discussed. J.M.C.

Research Work in the Leather Industry in France. Prof. Ch. Gastellu. *J. Soc. Leather Trades' Chemists*, **43**, 140–45 (1959).—A survey of the research in the leather industry in France dealing particularly with the Leather Industries Research Institute at Lyons. J.M.C.

Mold-proofing of Leather: A Comparison of Methods for Evaluating Mold Resistance. G. H. Green. *J. Soc. Leather Trades' Chemists*, **43**, 212–20 (1959).—A review is given of published methods of comparing fungicidal activities and of assessing the effectiveness of mold-proofing treatments. Experimentally, three test methods, differing in the method of innoculating the samples, were compared by using four fungicides. A new test method is proposed in which each sample is innoculated by pressing both surfaces gently against a piece of untreated molded leather. Samples are stored over 0.4% NaOH solution. Innoculation is repeated at intervals of 14 days in separate containers. The new test is said to evaluate both volatility as well as stability of leather fungicides. J.M.C.

Hydroxyproline as a Measure of Hide Substance. J. H. Bowes. *J. Soc. Leather Trades' Chemists*, **43**, 203–11 (1959).—A modified Neuman & Logan method for the determination of hydroxyproline in skins and beamhouse liquors is described. The hydroxyproline contents of various collagen preparations and of skins at various stages during processing are reported. A critical step in the determination, destruction of excess peroxide, is accomplished by heating at 40°C. for 15 min. Characteristic pink color is developed by heating at 70°C. for 30 min. in the presence of 0.8*N* H_2SO_4 as compared with 1.2*N* in original method. Recovery of hydroxyproline added to serum albumin followed by hydrolysis was 100 ± 1%: Ca^{++} interferes and is removed from hydrolyzates by adsorption to an ion exchange column. After surface washing and acetone-dehydrating, limed hides from several tanneries were sampled in the official position, and the hydroxyproline content was determined. Values ranged from 13.0 to 14.0% with an average of 13.5%. Hide substance in vegetable-tanned leathers calculated on the basis of hydroxyproline was 5 to 10% lower than when calculated on nitrogen content. J.M.C.

Aspects of Pigment Finish Formulations. W. O. Nutt. *J. Soc. Leather Trades' Chemists*, **43**, 197–203 (1959).—To obtain equivalent film properties and performance from different colors a system of finish control is required which correlates pigment volume content, thickness of deposited films, and the solids content of the finish at time of application. The formulation of finishes of known volume content is described, and procedures for utilizing pigment volume content and other factors in the production control of leather finishing are discussed. The effect of altering the charge of dispersed particles in pigment finishes and methods for obtaining desired effects by charge control are considered. J.M.C.

Investigations on Shoe Climate and Foot Comfort. G. Gran. *J. Soc. Leather Trades' Chemists*, **43**, 182–96 (1959).—Semiquantitative estimation of the relative humidity (R. H.) inside shoes worn under normal conditions is obtained by placing between sock and shoe small pieces of upper leather conditioned to equilibrium with air of various R. H. and then determining the change in weight of the pieces. A loss of weight indicates an R. H. inside the shoe lower than that to which the piece was conditioned and vice versa. The R. H. inside shoes worn indoors was found to range from 65% to 95%. Of the moisture escaping from the immediate vicinity of the foot, 40% is removed by the pumping action of the foot and shoe during walking, 50% is absorbed by the shoe materials, and the remainder penetrates the upper leather. The absorbed moisture is held equally by insole and upper leather portions of the shoe. J.M.C.

A Comparison of the Wear of Leather and Rubber Soles. G. Tóth and G. Tóth, Jr. *Bőr- és Cipőtechnika*, **8**, No. 3, 77–81 (1958); *Hung. Tech. Abstr.*, **11**, 18 (1959).—A wearing machine of novel design has been constructed with which the resistance to wear of both leather and rubber soles can be measured. The wearing force is measured by a dynamometer and the path of wear is also indicated. Since after frequent use the wearing surfaces soon become clogged with leather fibers, which at the same time reduces the volume of worn-off material, the wearing surface is constantly renewed in the new apparatus. The resistance to wear is characterized by the specific wearing work (the kg.-m. required of wearing off 1 cc. of material) which between certain limits does not depend on the load. The apparatus also measures the friction coefficient of pairs of materials. The friction coefficient of rubber soles is almost double that of leather soles. The specific resistance to wear of various rubber and leather goods is compared in a table proving that the finer the rubbing surface with which the determination is effected, the greater the specific wearing work. In analyzing the process of wear during walking the order of magnitude of the works done to overcome soil friction, air friction, soil compression etc. are estimated. Computations proved that with leather- and rubber-soled shoes of identical stiffness the difference between the friction work done in walking and the specific friction works can be considered as minimum within a certain range depending on the manner of walking. The tests are being continued.

Influence of Synthetic and Vegetable Tannins on the Tear Strength of Hide. G. Tóth and J. Ribli. *Das Leder*, **10**, 106–9 (1959).—It is well known that the strength of dry, untanned animal hide is greater than that of leather made from it, but Michailov (*The Chemistry of Tanning Materials and Processes*, Moscow) has found that the strength of individual fibers is increased by tanning. In leather the fiber bundles are not all loaded simultaneously. To determine if the strength of individual fibers could be imparted to leather, pieces were cut from an unhaired hide in the wet condition so all pieces would have the same number of fiber bundles, and were broken wet to avoid the change in lattice caused by drying. Sections of a croupon, completely delimed with $(NH_4)_2SO_4$, were each cut into 24 long narrow rectangles and numbered. The odd-numbered pieces were tested wet, untanned. Half of the even-numbered pieces were tanned in a 6°Bé solution of a syntan

for 2 weeks then tested wet directly from the tan liquor. The other half were tanned with syntan as above, then left for 4 weeks in an 8°Bé (sulfonated?) quebracho solution. Tannages were made with 16 different syntans, an auxiliary and a resin tannin, and 5 pure vegetable tannins. Some dried specimens were also tested; wet leather was about 30% stronger than the dry leather. The average wet tear strengths of the leathers, compared to the untanned skin, are shown in the following table:

Tanned with	Tear Strength %	Stitch Tear %	Continued Tear %
Exchange syntan	108	125	82
Vegetable tannin	115	126	81
Exchange and vegetable tannin	120	160	90
Not tanned	100	100	100

Auxiliary syntans did not increase strength. Exchange syntans were better the more they increased the strength of the hide during tanning. Pretanning with syntan resulted in more uniform deposition of vegetable tannin and therefore in stronger leather. The continued tear method gave low results. In this test the specimen is split to form 2 tongues, but without a punched hole at the end of the split. The tongues form small arcs near their junction where rupture is occurring; the arcs increase the lever arms and therefore decrease tearing load. Tanning stiffens the leather fibers and increases the arcs.

I.D.C.

The Purpose and Results of an Investigation of Factory Power Economy Based on an Example from the Leather Industry. H. Schaefer. *Das Leder*, **10**, 80–82 (1959).—By remodeling an older drier to increase drying temperature from below 40°C. to just below 50°C. and to lower relative humidity from about 40% to 30%, the time in the drier was reduced from 195 to 135 min., and the steam requirement was reduced from 2.56 kg. to 1.76 kg. per kg. of water removed. Leather quality was not lowered. In a test with fresh air at 13.5°C. and 83% relative humidity and vented air at 44.5°C. and 34% R.H., the fresh air brought in 41% and the leather 56% of the moisture that was vented. A heat balance showed that the air brought in 33% and steam 59.5%, and that the vented air removed 97.5% of the heat. The leather brought in and also removed about 1.5% of the heat.

I.D.C.

White Glove Leather. F. Elsinger. *Leder Kurier*, **2**, 51–59 (1958).—A review of the tanning materials and methods used for tanning white glove leather.

I.D.C.

One- and Two-Step Collagen-Gelatin Transformation in Alkaline and Acid Media. A. Küntzel and E. Heidemann. *Das Leder*, **10**, 49–57 (1959).—A one-step acid process for converting pigskins to gelatin has been patented and is in use in the U.S.A. An investigation was made to determine if the usual two-step lime process could be converted to a one-step process and also if a two-step acid process would be advantageous. The first step of the alkali method is a topochemical hydrolysis in which peptide chains are broken into shorter fragments without loss of skin structure; there is, however, some solution hydrolysis and loss of protein. The second step is a thermal denaturation or gelatinization. Thermal denaturation of unlimed skin causes contraction of the fibers, an increase in specific gravity, and a breaking of hydrogen bonds by melting, not by hydrolysis. The skin structure as a whole is changed irreversibly, although the form of single fibers can be restored by stretching. A two-step acid method was attempted with sulfuric acid (H_2SO_4) because it is divalent like lime. Flesh splits were treated with 10 times their weight of acid-salt solution at 15° and at 25°C., using 5, 10, 15, and 20% H_2SO_4 and 0, 5, and 10% salt. Time of treatment was adjusted to give optimum ripening as determined from preliminary tests and varied from 20 to 180 days. Cooking was done at 60°C. for 3 hr. in 300 ml. of water. The resulting gelatin was dried and weighed. Digestion time with acid was not shorter than with lime, and loss of protein was greater. The loss was 4.5% with 5% H_2SO_4 and 10% salt in a 180-day digestion at 25°C. After digestion for 100 days with 10% H_2SO_4 the loss of hide substance was 10.2% with 10% salt, 15.1% with 5% salt, and 23.2% with no salt. The loss in a comparable 96-day digestion with lime was 5.5%. The acid gelatin was clear but had a yellow-brown coloration caused by action of the acid on carbohydrate. The gel strength was high in relation to viscosity. The gelatin was of lower quality if acid strength was higher than 5%. Digestion with hydrochloric acid (HCl) was also investigated, varying time (0–26 days), temperature (10°–40°), concentration of acid (0.5–5.0%), and concentration of salt (0–20%). Optimum yield was found with 2.5% HCl and 5% salt at 35°C., but HCl was not as good as H_2SO_4. The optimum pH for the one-step acid process was found to be 1.5–1.95. This process, which is used on pigskins, will also yield gelatin from fresh cattlehides. Substituting NaOH for HCl in this process did not yield gelatin. In general the results show that acid is not as suitable for the two-step process as alkali, especially lime. Acid causes greater loss of material without shortening the time for topochemical hydrolysis. Acids are more suitable for the one-step process because HCl lowers shrinkage temperature of collagen through a strong swelling effect and also favors swelling at higher temperatures which makes solution of the collagen easier. Acid concentration can be kept low enough so that decomposition of the gelatin in solution can be ignored. Alkali, in the higher temperature range, causes much less swelling than acid, and the gelatinization temperature is not lowered appreciably. I.D.C.

Increasing the Water Resistance of Leather (Upper) by Use of Aluminum Soaps. O. Rodziewicz and J. Kraft. *Leder Kurier*, **2**, 230–5 (1958).—Water resistance of leather is obtained by (1) depositing tannin or filling material between the fibers, (2) retaining the ability of the fibers to swell in water, and (3) treating the leather chemically or physically to increase its density. Upper leather owes its small water absorption to the presence of about 20% of fat and to other hydrophobic substances, one of which may

be a metal soap. The best soaps, on the basis of plasticity and resistance to aging, were aluminum oleate and ricinoleate. Deposition of metal soaps in the leather from emulsions or organic solvents was not very satisfactory. The best leather was made by retanning a vegetable-tanned leather with an aluminum or chromium salt, then treating with the sodium salt of a fatty acid to form the aluminum soap *in situ*. The process, however, is not simple and requires various adjustments. Special consideration must be given to choice of metal salt, presence of neutral salts in the tan liquors, and the neutralization process. Best results were obtained by retanning with a basic aluminum salt in a short float, washing, wringing, then oiling "dry" with a mixture of fat and sodium ricinoleate. Analysis showed that the extracted "fat" contained 15–20% of the total Al_2O_3. After extraction with petroleum ether, the leather contained about 20% of bound fat. In general, aluminum retannage results in an increase in shrinkage temperature and in a binding of aluminum to hide protein through the combined vegetable tannin. Water resistance of leather is increased by the mixture of fat and aluminum soap which increases density and makes the leather more hydrophobic. At the same time the sodium soaps do not destroy the ability of the hide fibers to swell in water. I.D.C.

Studies of the Reactive Groups of Collagen. III. Methylation and Guanidination. K. Thomas Joseph and S. M. Bose. *Bull. Central Leather Research Inst., Madras*, **5**, 388–411 (1959).—Collagen was methylated by 7 different methods, and the products were analyzed for methoxyl and free amino groups.

Methylating agent	Millimols per g. collagen	
	Methoxyl	Free NH_2
Diazomethane in acid 85% ethanol	0.50	0.27
Trimethyl phosphate (10 treatments)	0.74	0.05
Dimethyl sulfate (10 treatments)	0.71	0.04
Methanol-HCl	0.82	0.30
Methyl iodide (14 days)	0.21	0.30
Methanol and thionyl chloride	0.78	0.36
Methanol and ethyl chloroformate:		
treated 3 days	0.84	0.43
treated 5 days	0.86	0.54
No treatment	0.05	0.37

The last two processes are preferred, because of completeness of methylation of carboxyl groups and absence of action on amino groups. The increase in free amino groups brought about by methanol and ethyl chloroformate is shown to be caused by an N-O-acyl shift at serine and threonine linkages to give corresponding O-peptidyl esters with free amino groups, as previously found by Elliott (*Biochem. J.*, **50**, 542 [1952]) for silk fibroin. This reaction is largely reversed by treating the methylated protein for 5 hr. with borate buffer at pH 9. Free amino groups were determined by the DNP procedure with the following results:

Substance	Collagen methylated with methanol and ethyl chloroformate for 5 days	Same, treated with borate buffer at pH 9 for 5 hr.
	millimols per g. collagen	
Free amino groups	0.54	0.40
DNP aspartic acid	0.014	0.013
DNP serine	0.052	0.012
DNP threonine	0.048	0.008
DNP alanine	trace	0.007
DNP glycine	0.013	0.014

Guanidination of ε-amino groups was done with O-methyl isourea neutral sulfate as described by Roche *et al.* (*Bull. Soc. Chim. Biol.*, **36,** 85 [1954]). Completeness of guanidination was calculated from the decrease in free amino groups and increase in arginine in the hydrolyzed protein. Both determinations showed that guanidination was about 65% complete. H.B.M.

Manufacture of Kattai and Bunwar Leathers. T. S. Krishnan, K. Rajabathar, and K. T. Sarkar. *Bull. Central Leather Research Inst., Madras,* **5,** 412–21 (1959).—These are vegetable-tanned, buffed leathers, made on calf or light hides respectively. Procedures are given for manufacturing these types of leather from raw stock and from E.I. tanned stock. H.B.M.

Investigations on Fire and Explosion Hazards and Safety Precautions for Automatic Leather Spraying and Drying Equipment. G. Schön and C. H. Degener. *Das Leder,* **10,** 58–65 (1959).—Four types of combined spray coloring and drying machines are described. The solvent composition, ignition temperature, and explosion limits are given for several dye preparations. Air velocities in the machines were measured with an anemometer, and vapor concentrations were determined both with an interferometer and by chronometric analysis. In the latter method the mixture for analysis is pulled through a tube containing a granular indicator specific for the given vapor. Data for certain operating conditions are shown in curves. Exhaust or ventilator fans must keep k (where k is the ratio of vapor concentration in the air mixture to lower explosion limit) below 0.5 even when maximum amounts of spray solution are being used. The exhaust vents should be located so they are not affected by wind. Air velocity in all parts of the spray section should be the same. The spray pistol and the exhaust fan should be connected so that the pistol cannot be used unless the fan is in operation, and the fan should run for 30 min. after the pistol is shut off. The volumes of the spraying and drying sections should be as small as possible, and all openings should be small. The trough for collecting the dye solution should have enough slope for good drainage. The heater should be over the spray section so dust will not deposit on it and ignite. All parts should be cleaned regularly to prevent accumulation of dye residues. Electrical fixtures should comply with specifications for explosion-proof equipment. All other sources of ignition should be avoided. The distance between the spraying and drying sections should

be not more than 20 cm. to avoid entrance of vapors into the workroom. The workroom should be aerated to have a slight excess pressure. There should be an outside cutoff for the entire plant except ventilators. The minimum capacity of the exhaust fan, Q_1, in m^3/min., to avoid entrance of vapor into the workroom, can be calculated from the equation: $Q_1 = F\ v\ 60\ z$, where F is the area of all openings in m^2, v is the air velocity in m/sec. (it should be at least 2), and z is a safety factor (for example 1.2). The minimum fan capacity to prevent accumulation of a dangerous amount of explosive mixture in either the spray or drying section is given by the following equation: $Q_2 = G_{max}\ (273 + t)\ /k_z\ U\ 293$, where G_{max}, in g/min., is the maximum amount of solvent evaporated per min., t is the maximum air temperature, U is the lower explotive limit in g/m^3, and k_z is the safety factor by which the exhaust air vapor concentration is below U. k_z should never be above 0.5. I.D.C.

Raw Hide and Raw Hide Preservation. Richard Würtenberger. *Leder Kurier*, **3**, 67–69 (1959).—Present curing methods are reviewed briefly. An increase in leather yields can be obtained by the Oraskin salting process which fixes in the hide the unstructured proteins such as procollagen and protocollagen, proteins made soluble by enzymes, etc. In one test, leather yield was 107.4% from hides cured by the Oraskin process, or 112.8% if the hides were pretreated with calcium chloride before the Oraskin salting, as compared with 100% yield for leather from hides cured by the normal naphthalene-soda salting process. I.D.C.

Sole Leather Tanning in Warm Wattle Extract Liquors of Constant Concentration. S. G. Shuttleworth. *Das Leder*, **10**, 97–101 (1959).—A closed tanning system has been developed using circulating liquors of uniformly high concentration at 35°C. This process has solved the problem of tanning the offal pieces. Maintaining strength of the strong liquors is made possible by addition of extract and by regular withdrawal of a portion for use in coloring (rocker) liquors. Accumulation of salts, sugars, slime, and sludge in the liquors is prevented by the use of two 20° Bk. coloring liquors and discarding them after the second use. Semitechnical tests were made on lots of 60, 23 x 33 cm. pieces of hide in iron tanks lined with Fiberglas and polyester, and with temperature control to 0.1°C. Scales were mounted above the vat so weight gains could be followed accurately. Tannin penetrated the pieces from an 80-lb. hide in 6 days at 20°, in 4 days at 30°, and in 3 days at 35°C. A 60-lb. hide was penetrated one day earlier. Weight gain was greater at 35° than at 20° and was a maximum in about 3 days. Average weight yields of the pieces were 204.7% (dry-leather weight as % of unhaired-hide weight) at 20°, 215.6% at 30°, and 226.6% at 35°C. The higher temperature was without influence on color and grain but was significant for firmness and elasticity. Tanning time could be further decreased from 11 days to 6 days by raising the temperature of the lime and bate liquors to 35°C., and at the same time leather yield and quality were improved. The Lira (Leather Industries Research Inst.) process is outlined. In brief, this method is as follows: Wash wet-salted hides with 35° water in a clean drum, remove hair with 1.5% Na_2S in a minimum volume of water, wash out pulped hair after 1 hr., lime with 3% lime and 100% water, turning the drum 5 min. each hr.; on the second day, flesh and set out, hang in a lime liquor containing 0.5% NaOH

for 6 hr., rinse, tie on sticks and hang in a pickle containing 2.5% calgon, 5% NaCl, and 1.5% H_2SO_4; on the third day, hang in the weak, once-used liquor for 5 hr., in the fresh coloring liquor for 5 hr., then for 3 days in the closed system with 100° Bk. liquor. The above process is to be conducted at 35°; at ordinary temperature the times must be doubled. For firmer leather the time in the system should be increased from 3 days to 6 days. All tan liquors should contain 0.5% calgon to fix the pH value. The second-day lime liquor should be strengthened daily with 0.5% NaOH and renewed weekly. To the deliming pickle there must be added daily enough salt to restore the original Barkometer strength, 1.25% calgon, and acid to bring the pH to 2.5. Less calgon is used in this process than in the usual drum rapid tannages, and there is no expense for deliming acid. Calgon counteracts the gray shade of the leather caused by iron. I.D.C.

Study of Fatty Resinoid Exudations on Fatliquored Leather. Dr. Ch. Gastellu and I. Jullien. *Bulletin de l' Association Francaise des Chimistes des Industries du Cuir*, **21,** 26–31 (1959).—Dr. Gastellu makes a distinction between white and resinoid exudations. The former do not alter the leather, but the latter detract from its appearance. The latter appear in the form of fine droplets which become larger and larger at the surface of the leather. If this phenomenon occurs when the leather is in piles, the leather sticks together, and it is impossible to separate it without damage. Experiments on fatliquoring were made on chrome-vegetable leather which is more subject to resinoid exudation than vegetable-tanned leather. The influences of oil acidity, leather acidity, antiseptics, and mineral oil were studied successively. The first three factors did not have any influence on the formation of exudations, which in all cases developed with the same rapidity and in about the same quantity. On the other hand, all leathers in which the fatliquoring contained mineral oil remained free of resinoid exudations. R.H.

Study of the Tanning of Shoulders for Vegetable Chrome Insoles. Dr. Ch. Gastellu and I. Jullien. *Bulletin de l' Association Francaise des Chimistes des Industries du Cuir*, **21,** 11–15 (1959).—The object of this work is to study the influence of the chromic oxide content and of vegetable tanning on the properties of vegetable chrome insoles. A series of experiments were made on shoulders from cows, the experiments being divided into three groups. In each of these groups three retannages were applied with 20, 30, and 40% extract of chestnut at pH 5. The results of chemical analysis and physical tests were as follows: (1) All the leathers retanned with a 20% extract were not completely penetrated by the tannin. (2) All the leather tanned with only 1.0% chromic oxide seemed more or less flat, even in the case of 40% extract retannage. (3) The leathers tanned with 1.5 and 2.0% chromic oxide and retanned with 20% extract were flat, and their currying presented some difficulty. (4) The other leathers, that is, those which have received a chromic oxide tannage of 1.5% and 2.0%, and a 30.0% and 40.0% extract retannage were satisfactory. (5) The content of soluble mineral matter is about 2.0% and consists of sodium sulfite and bisulfite or similar ammoniacal salts. (6) The soluble chrome content can be reduced to small amounts by washing the leather after tannage. R.H.

PATENTS

Lignin Sulfonate-Phenol-Formaldehyde Tanning Extract and Process of Making Same. U. S. Pat. 2,891,020. J. L. Barren, Port Allegany, Pa., assignor of one-third to Emporium Trust Company, Emporium, Pa., and one-third to Horace E. Allen, Longmeadow, Mass., both as trustees. Appl. January 24, 1957.—1. In a process for making a tanning extract, preparing a first reaction mass containing from about 7% to about 21% by weight of lignin sulfonate solids and a phenol-formaldehyde mixture consisting of from about 40 parts to about 44 parts of phenol, and from about 6 parts to about 8.5 parts of formaldehyde, all in an aqueous medium, said lignin sulfonate solids and said phenol-formaldehyde mixture comprising from 40% to 75% of the total weight of said mass, reacting this mass at a temperature of from about 165°F. to about 175°F. under conditions of violent agitation, preparing a second reaction mass comprising an aqueous solution consisting of from about 30% to about 66% water and from about 30% to about 56% of unreacted lignin sulfonate solids, adding from about 4% to about 16% of the product of said first reaction mass, and reacting said second reaction under conditions of agitation and at temperatures of from about 165°F. to about 175°F.

Powdering of Natural Waxes. U. S. Pat. 2,878,270. C. J. Ish, Columbus, Ohio, assignor by mesne assignments, to Pennsalt Chemicals Corporation, a corporation of Pennsylvania. Appl. December 30, 1955.—1. The method of powdering natural waxes comprising treating the wax to the action of anhydrous hydrogen fluoride and removing the anhydrous hydrogen fluoride therefrom at a temperature below the melting point of the wax to yield a powdered friable wax, said natural wax selected from the group consisting of animal waxes, vegetable waxes, and ester mineral waxes. Suitable for use in leather dressings, polishes, sizings, or adhesives.

Coated Leather. Brit Pat. 811,502. Imperial Chemical Industries Ltd. Appl. June 22, 1956.—Leather is coated with a pigmented water-based finish containing dispersed therein poly-β-ethoxyethyl methacrylate and dimethyl phthalate, which is then dried to leave a nontacky finish which may be plated or embossed. Specification 769,694, [*Group* IV (a)], is referred to.

Process for Preparing Vinyl Tin Compounds. U. S. Pat. 2,873,287. H. E. Ramsden, Scotch Plains, N. J., assignor to Metal & Thermit Corporation, New York, N. Y., a corporation of New Jersey. Appl. May, 9, 1956.—1. In a process for the preparation of a vinylic tin compound which comprises reacting a vinylic magnesium chloride compound with a tin compound having a tin atom bonded to at least one halogen atom, the step which comprises carrying out the reaction in the presence of at least one mole of a cyclic ether for every mole of vinylic magnesium chloride used, said cyclic ether being selected from the class consisting of tetrahydrofurans, tetrahydropyrans, dihydropyrans, and N-methylmorpholines, with the further restriction that said cyclic ethers contain not more than one double bond in the ring and that at least one carbon atom adjacent the oxygen atom in said cyclic ether is free of any substituents other than hydrogen. Compound useful as a preservative for leather.

Process for the Preparation of Vinyl Tin Compounds. U. S. Pat. 2,873,288. S. D. Rosenberg, North Plainfield, and A. J. Gibbons, Jr., East Brunswick Township, Middlesex County, N. J., assignors to Metal & Thermit Corporation, Rahway, N. J., a corporation of New Jersey. Appl. September 18, 1956.—1. The procese of preparing monovinyltin trihalides, divinyltin dihalides, and trivinyltin monohalides by a disproportionation reaction comprising mixing stoichiometric amounts of a halide selected from the class consisting of tin tetrahalide, divinyltin dihalide and vinyltin trihalide, with a vinyltin compound selected from the class consisting of tetravinyltin, divinyltin dihalide, and trivinytin monohalide, said halide being selected from the class consisting of chlorides and bromides to yield the stoichiometrically determined vinyltin halide, wherein when said halide is a vinyl trihalide, said vinyltin compound is selected from the class consisting of tetravinyltin and trivinyltin monohalide, and wherein when said halide is a divinyltin dihalide, said vinyltin compound is tetravinyltin. Product useful as a preservative for leather.

Dyeing of Leather. U. S. Pat. 2,893,811. J. S. Kirk, East Greenbush, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware. Appl. December 30, 1955.—1. In a process for dyeing leather which has been tanned with a member of the group consisting of vegetable tanning agents and aqueous solutions of formaldehyde and a polyhydric phenol of the group consisting of resorcinol and pyrogallol. the improvement comprising dyeing such leather with a direct dyestuff from an aqueous dyebath at a pH of about 5½ to 7 containing about 0.1 to 5%, based on the weight of the leather, of a water-soluble non-ionic surface-active agent having the formula $R—NH—(CH_2CH_2O)_nH$, wherein R is a straight chain aliphatic hydrocarbon radical of from 16 to 18 carbon atoms and *n* has a value of about 12 to 18.

Simultaneous Filling and Tanning with Resin Dispersions. Brit. Pat. 811,694. Imperial Chemical Industries Ltd. Appl. April 16, 1958.—Hides and skins are simultaneously filled and tanned with an aqueous dispersion of a water-insoluble solid copolymer of an ester of methacrylic acid with a polymerizable aldehyde or a derivative from which the parent aldehyde is recoverable by hydrolysis. The *p*H is preferably 7.5–8.5 during the penetration of the hide or skin followed after complete penetration by adjusting the *p*H to below 4 or above 9. Specified esters of methacrylic acid are ethyl, propyl and preferably methyl. Specified aldehydes are crotonaldehyde, acrolein, methacrolein and the acetal and acetate derivatives thereof. The copolymer may optionally contain minor amounts of acrylic or methacrylic acid, amide or nitrile. The proportion by weight of aldehyde or derivative in the copolymer may be up to 20 per cent and preferably 2–10 per cent. Tanning may be completed by chrome tanning.

Coating Leather with Polyamides. Brit. Pat. 811,696. Badische Anilin- & Soda-Fabrik A.G. Appl. May 15, 1957.—A process for finishing leather with a polyamide coating consists in using a polyamide which has been prepared from (1) 15 to 85 parts by weight with reference to the entire polyamide-forming initial material of diamine normally used in polyamide formation and

the equimolar amount of a dicarboxylic acid of which the carboxylic groups are connected by a chain of 6–12 carbon atoms, the said chain containing a lateral branch of 7–10 carbon atoms; and (2) 85 to 15 parts by weight of compounds usually used for forming polyamides. The coating may be applied in solution in an alcohol preferably with from 1–4 carbon atoms to unbottomed leather or to a bottoming of pigmented polymer or collodion coating layers or polyamide coating layers which may be pigmented with collodion coating colours, the solution being compatible with the usual diluents and varnish solvents. The polyamide solutions are compatible with nitrocellulose solutions and collodion pigment finishes. Specified acids in (1) are l-nonyl-octane dicarboxylic acid-(1:8) and 1-octyl-nonane dicarboxylic acid-(1:9). Specified amines are 4:4'-diaminodicyclohexyl, 4:4'-diaminodicyclohexylmethane, which are preferred in (1) and ethylene diamine, tetramethylene diamine, octamethylene diamine, decamethylene diamine, hexamethylene diamine, l-aminopropanol-(3) and metaphenylene diamine. Specified acids in (2) are adipic, sebacic, suberic, decamethylene dicarboxylic and heptamethylene dicarboxylic acids, and their derivatives capable of polyamide formation. The diamines and dicarboxylic acids may be added as a salt formed by interaction or by themselves. Lactams such as caprolactam, oenanthlactam and caprylic lactam may be present in (2).

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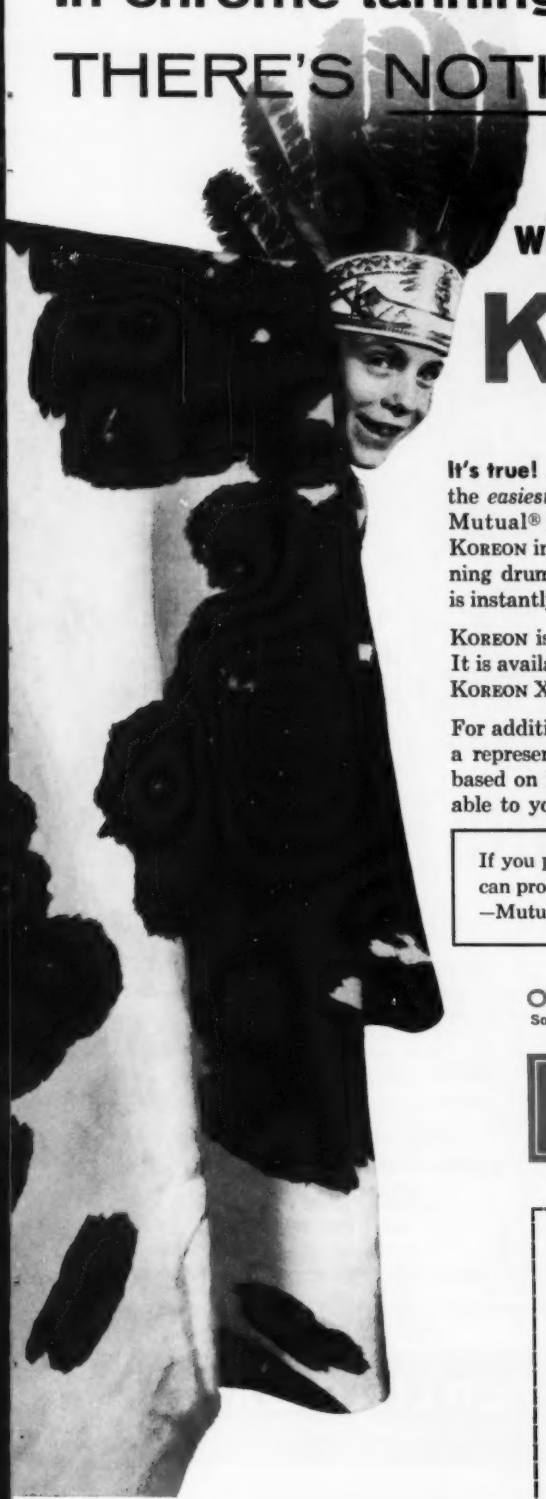

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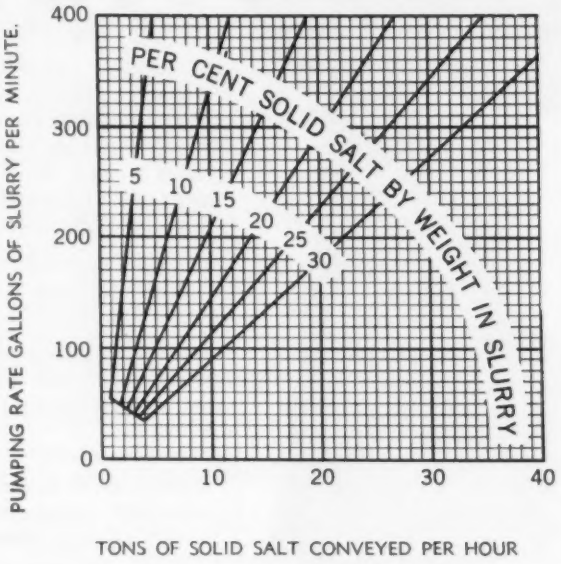

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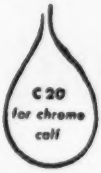

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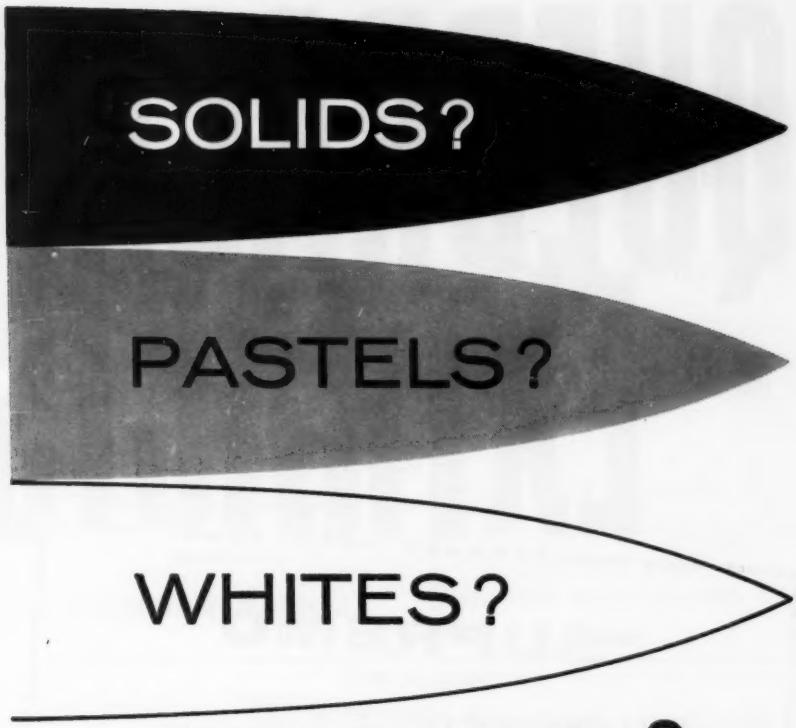

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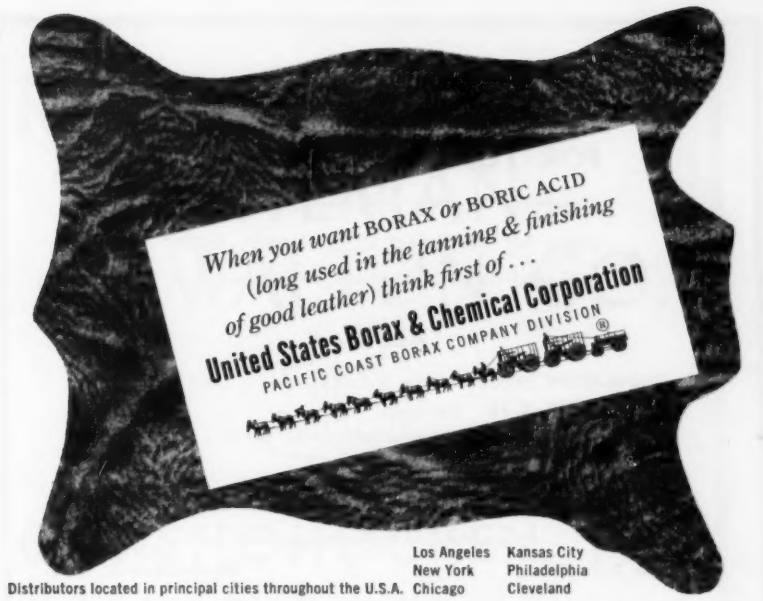
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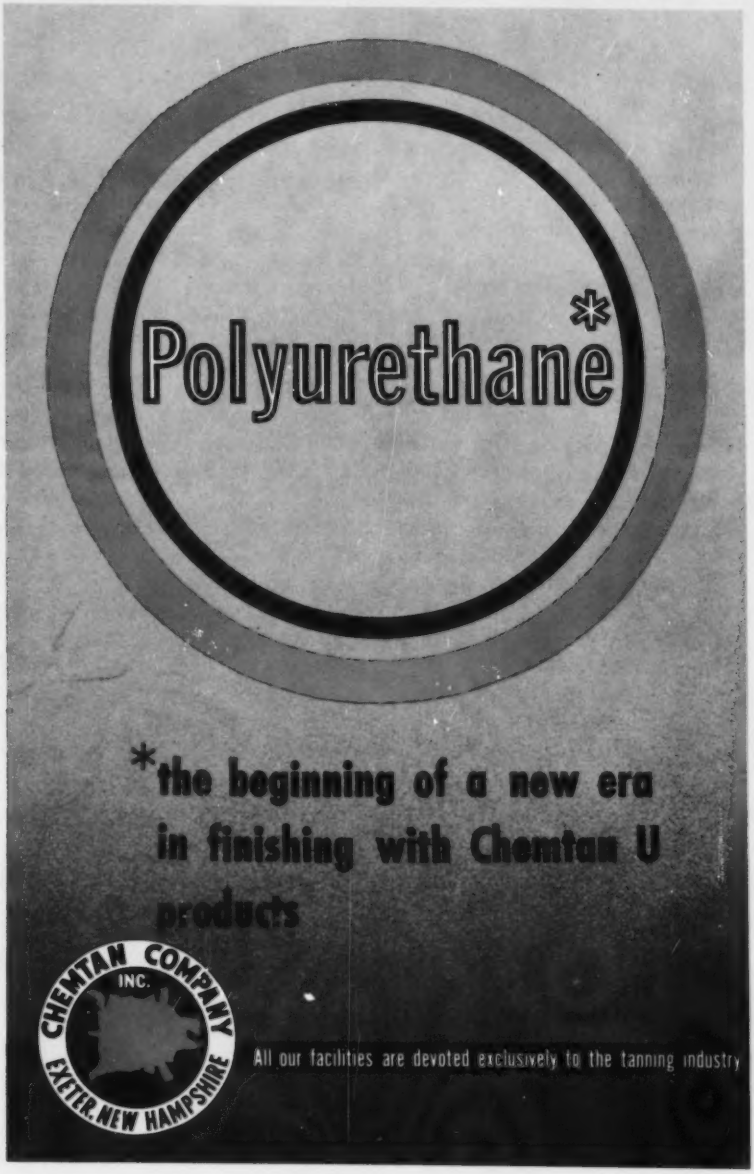
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